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AN X-RAY SEARCH FOR THE ORIGIN OF FERROMAGNETISM

By J. C. Stearns
Ryerson Physical Laboratory, University of Chicago

(Received November 19, 1929)

Abstract

A sensitive null method, employing two crystals and two ionization chambers, was used to detect any change in intensity of an x-ray beam reflected from a magnetic crystal, when this magnetic crystal was magnetized. This method was capable of detecting from 1.0 to 0.1 percent change in intensity, according to the intensity of the reflected beam. Crystals of magnetite and silicon steel were used. No change of intensity was observed, although the theoretical change was several times that which could have been detected. The change in intensity of the x-ray beam was computed on the basis of the alteration of the structure factor due to orientation of electronic orbits by the magnetic field. It is concluded that electrons revolving in orbits within the atom cannot account for ferromagnetism. The models of Honda and Ehrenfest are briefly discussed. On the basis of present atomic models and present experimental evidence it appears that the ultimate magnet should be identified with the spinning electron.

SEVERAL experiments have been reported[1] in which x-rays have been used to study the nature of the ultimate magnetic particle. From these it has been concluded that the most minute crystal aggregations in solid iron are not oriented by a magnetic field, that the ultimate magnet cannot be a group of atoms such as the chemical molecule, and finally, that the atom as a unit cannot account for ferromagnetism. On the basis of present atomic models three possible ultimate magnetic particles remain: the atomic nucleus, the spinning electron, or electrons revolving in inner orbits. The following experiment was performed primarily to ascertain whether electrons revolving in the inner orbits may be responsible for ferromagnetism.

The Experiment

The apparatus used is indicated in Fig. 1. It is essentially a refinement of that employed by A. H. Compton and Rognley. The x-ray tube had a water-cooled molybdenum target, and could be operated at 35 milliamperes

[1] M. de Broglie, Le Radium **10,** 186 (1913). K. T. Compton and E. A. Trousdale, Phys. Rev. **5,** 315 (1915). A. H. Compton and Oswald Rognley, Phys. Rev. **16,** 464 (1920). T. D. Yensen, Phys. Rev. **31,** 714 (1928).

and 50 kilovolts. One portion of the x-ray beam fell on C', a crystal of magnetite or silicon steel, which reflected the $K\alpha$ line into ionization chamber I'. Another portion of the beam passed above C' and was incident upon C'', a calcite crystal, from which the $K\alpha$ line was reflected into chamber I''. The electrodes of the ionization chambers were connected to the same pair of electrometer quadrants, while one chamber was maintained at a positive and the other at a negative potential. S' and S'' were adjustable slits. An intense beam of x-rays was allowed to fall upon the crystals, and the slits were adjusted until the electrometer charged up at a very slow rate. With other conditions unaltered the crystal C' was magnetized and the rate of deflection of the electrometer again taken. In order to make a comparison of successive readings, two readings taken with the electromagnet unenergized alternated with two successive readings with the magnet energized. From a set of twenty-five to fifty readings for each order the mean change of

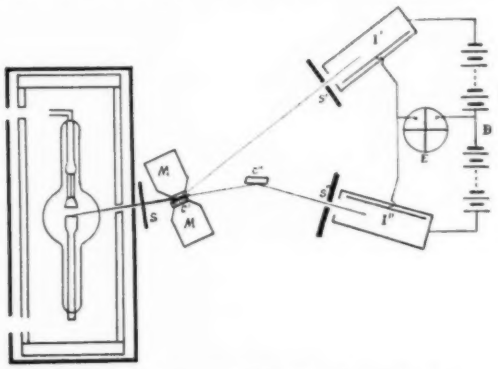

Fig. 1. Diagrammatic sketch of apparatus.

rate due to magnetization was determined. A sheet of aluminium, which absorbed four percent of the beam was then placed in front of S' and the resulting change in the rate at which the electrometer was being charged observed. Then: Change of rate due to magnetization/Change in rate due to absorption by aluminium $\times 4$ = percent change in intensity due to magnetization.

The electromagnet M had a laminated core about which were wound five thousand turns of number 23 copper wire. The air gap was about 2 mm. Demagnetization was secured by successively reversing and gradually decreasing the current. The magnetic induction was measured by means of a commercial flux meter. The calcite crystal was fixed to a non-magnetic mounting which was placed outside the magnetic field and could be rotated independently of the electromagnet and the magnetic crystal. The x-ray tube was mounted inside a heavy wrought iron pipe, the ends of which were closed by iron plates one inch in thickness. The ionization chambers were duplicates, and each was filled with argon.

Disturbing Effects and Their Elimination

It was necessary to mount the crystal C' with unusual care in order to avoid motion of the crystal relative to the incident beam when the magnet

was energized. It was found also that the establishing of the magnetic field sufficient in strength to produce magnetic saturation in the crystal shifted the electrometer needle through several degrees, and changed the current sensitivity of the electrometer. By using a mica needle plated with a suitable combination of gold and platinum this effect was overcome. In testing the sensitivity the deflection rates were compared with and without the magnetic field, using radium emanation tubes as a source of ionization.

Before the tube was enclosed in the iron pipe, the field in the region of the x-ray tube was found to be sufficient to move the focal spot 0.2 or 0.3 mm. This shift produced a change in the intensity of the reflected x-rays of the order of 1 percent, which changed in sign with a reversal of the field. When the tube was placed in the iron pipe, tests showed the shielding to be adequate.

Calculation of Change in Reflection Due to Orientation of an Electron Orbit

The following method was used in computing the theoretical change in the intensity of the reflected beam due to K or L electrons being oriented by an external field so that their magnetic moments were parallel to this field. A. H. Compton[2] shows that

$$W_n = KF_n^2, \tag{1}$$

where W_n is the total energy diffracted by a small crystal and F_n is the structure factor of the atom, while the subscript n refers to the order in question, and K is a factor of proportionality. If the primed letters refer to the energy and structure factor respectively when the crystal is magnetized and the unprimed letters to the same quantities when the magnetic crystal is unmagnetized, then

$$\frac{W'}{W} = \frac{(F_n')^2}{(F_n)^2} = \frac{[F_n + (F_n' - F_n)]^2}{(F_n)^2} = 1 + \frac{2\Delta F_n}{F_n}. \tag{2}$$

neglecting higher powers of ΔF_n. To calculate the change in intensity it is thus necessary to know the number of atoms affected by the magnetic field and the structure factors of the atom for the order in question when the crystal is magnetized and unmagnetized respectively.

The structure factor[3] for the nth order of an electron moving at random over the surface of a spherical shell of radius r is

$$F_{en} = \frac{\sin 2\pi nr/D}{2\pi nr/D}, \tag{3}$$

where D is the grating space of the crystal. If magnetizing the crystal perpendicular to the reflecting face causes the orbit of an electron to lie in the plane of the reflecting face, its structure factor becomes unity, since the waves reflected by it are in phase with those from the middle of the atomic

[2] A. H. Compton, "X-rays and Electrons" p. 125.

[3] Reference 2, p. 148.

layer. If without the magnetic field the orientation of the orbit is random, then

$$\Delta F_{en}=1-\frac{\sin 2\pi nr/D}{2\pi nr/D}. \tag{4}$$

If, however, the crystal is magnetized parallel to the reflecting face, and the electron in question moves in a circle whose plane is perpendicular to the reflecting face, the structure factor for this electron becomes a Bessel function of the zero order,

$$F_{en}'=J_0(2\pi nr/D). \tag{5}$$

ΔF_{en} is then found in the same manner as in the preceding case.

If ΔF_{en} is the change in structure factor for each electron whose orbit is turned by the magnetic field, and if f is the number of electronic orbits per atom thus turned, the average change in structure factor is

$$\Delta F_n=f\Delta F_{en}. \tag{6}$$

From Eq. (2) it follows that the ratio of the intensities when the crystal is magnetized and unmagnetized respectively is

$$(W'/W)=1+2f(\Delta F_{en}/F_n). \tag{7}$$

To find the ratio f of the number of orbits oriented to the number of atoms, we may assume that each electronic orbit has a magnetic moment of one Bohr magneton. This ratio then becomes

$$\frac{1}{5589}\times\frac{\text{saturation intensity of magnetization}}{\text{number of atoms per molecule}}\times\frac{\text{molecular weight}}{\text{density}}.$$

On this basis, in the case of magnetite, half of the atoms will have one atom oriented, i.e. $f=0.5$ while for silicon steel three orbits per two atoms will be turned around, i.e. $f=1.5$.

The structure factor F_n of the atom for any order may be determined if the structure factor for the first order is known and if the relative intensity reflected in each order is known. Equation (1) could then be used to give the structure factor. The ratio Z/F of the atomic number to the structure factor for the first order does not vary greatly with different atoms. In the cases of sodium and chlorine this ratio is 1.45 and 1.25 respectively. It is thus reasonable to assume the structure factor for the first order of the iron atom to be about 20 and that of the oxygen atom to be about 6.5. The intensities for the first three orders from the 110 planes of iron have been measured, thus permitting direct substitution* in (1) to find the atomic structure factor for orders 1 and 2. In the case of magnetite we may make use of the fact that the experimental values of F, for reflecting planes that are similar and similarly placed, are experimentally found to vary approximately inversely as the order. In computing the results for magnetite it has accordingly been assumed that $F_n=20/n$ for the iron atom and $6.5/n$ for the oxygen atom.

* In making this substitution it is necessary to note that the factor K of Eq. (1) includes the trigonometric factor $(1+\cos^2 2\theta)/\sin 2\theta$ (cf. A. H. Compton, reference 2).

For silicon steel these considerations are sufficient for determining $\Delta F_{cn}/F_n$; but for magnetite it is necessary to know how a change in atomic structure factor will affect the intensity when the planes are neither similar nor similarly placed. Bragg[4] has shown that the 110 planes may be represented by a single plane having a weight

$$56+112\cos\pi n/4+168\cos\pi n+128\cos\pi n/2,$$

where n is the order of the spectrum. The first three terms are the contributions due to the iron atoms, while the last term represents the contribution of the oxygen atoms. One may assume that both the oxygen and iron atoms are affected by the magnetic field or that either the iron or oxygen atoms have their electronic orbits oriented by the applied field. The first assumption seems the more reasonable and is the one here employed. It is seen that in the fourth order the planes made up of oxygen atoms cooperate with those made up of iron atoms, and a maximum change in intensity would result if only the oxygen atoms were influenced. This is due to the fact that the change in intensity per oxygen atom is greater than that per iron atom and the total number of atoms affected in either case must be the same. If only the iron atoms were influenced the effect would still be detectable, while the result given in the table is that based on the assumption that both iron and oxygen atoms are turned about by an external magnetic field. In the case of the fifth order all the planes may be represented by a plane of iron atoms of weight 90. In the sixth order all the 110 planes may be replaced by planes or iron atoms of weight 224 with planes of oxygen atoms of weight 128 midway between the iron planes. If both kinds of atoms are affected by the magnetic field the change in intensity would be too small to detect, while if the inner orbits of the iron atoms alone are oriented there should be a detectable increase in the intensity of the reflected x-ray beam. On the other hand a change in the oxygen atom alone should produce a decrease in intensity which would have been detected. Thus, by considering the fourth, fifth and sixth orders of magnetite, all possible cases have been considered, and the magnitude of the theoretical effect found is great enough for detection by the method employed whichever atom is affected by the magnetic field. The radii used for the K and L orbits were computed by use of Bohr's formula.

It appears that any reasonable assumptions regarding atomic structure factor or magnetic moment per electron orbit must lead to a predicted effect of the order of magnitude here calculated.

Experimental Results

In the following table both the theoretical and experimental results are given. In the first column on the left the order is given. In the next column is given the theoretical ratio, $I'/I(K)$, of the integrated intensities reflected by the crystal when it is magnetized and unmagnetized respectively, assuming that the K electrons are the ones that orient themselves when the field is applied. In the next column is the same ratio for the case of the L electrons, while the last gives the experimental value.

[4] W. H. Bragg, Phil. Mag. **30**, 305 (1915).

TABLE I. *Ratio of x-ray reflection from magnetized to that from unmagnetized crystals.*

Order	Calculated I′/I(K)	Calculated I′/I(L)	Experiment I′/I
1. Magnetized perpendicular to the reflecting face			
		Magnetite (111) Plane)	
1	1.0000	1.0000	
2	1.0000	1.0003	1.0001+.0002
3	1.0006	1.0020	0.9999+.0002
4	1.0070	1.0230	0.9998+.0001
5	1.0015	1.0100	1.0002+.0001
6	1.0030	1.0210	1.0001+.0004
7	1.0050	1.0280	0.9988+.0015
		Silicon steel (110 Plane)	
1	1.0000	1.0012	1.0001+.0001
2	1.0009	1.0100	0.9999+.0001
2. Magnetized parallel to the reflecting face			
		Magnetite (111 Plane)	
4	0.9980	0.9100	1.0002+.0010
5	0.9970	0.8900	0.9997+.0004
6	0.9950	0.8000	1.0004+.0003
		Silicon steel (110 Plane)	
2	1.0000	0.9993	1.0003+.0006

In the above table the probable error of the mean is quoted.

It will be seen that the apparent changes in intensity of x-ray reflection due to magnetization are very small, and are of the magnitude to be expected from the probable error. There is thus no evidence for any change whatever in the reflecting power of these magnetic crystals due to magnetization. This conclusion is a considerable extension of the negative result of A. H. Compton and Rognley, for whereas in their experiments magnetite only was used, and this was magnetized only to one third saturation, here both the magnetite and the iron crystals were magnetically saturated. Moreover, these authors gave 1 percent as the precision of the experiment, whereas the more precise of the present experiments may probably be relied upon to 0.1 percent.

SIGNIFICANCE OF THE NEGATIVE RESULTS

Compton and Rognley[1] pointed out that a change of intensity of less than one percent in the fourth order when the crystal was only one third saturated was to be interpreted as meaning that the ultimate magnetic particle could not be the molecule or the atom as a whole unless the atom is surprisingly isotropic. The present data set a lower limit to the maximum displacement of atoms from their normal positions which could have occurred due to magnetization without being detected by this experiment. This distance could not have changed by as much as 1/2000 of the grating space without producing an effect that would have been detected by this experiment. It is also very improbable that the electrons revolving in inner orbits can account for ferromagnetism. In the fourth order in the case of magnetite the theoretical value is 35 times the experimental value, while in the second order for silicon steel the theoretical value is 9 times the experimental change.

Honda[5] ascribes the magnetic property of an atom to the nucleus. Within the nucleus he pictures electrons and protons as revolving in opposite senses. This gives a large magnetic moment and a small angular momentum which would enable the nucleus to be oriented by an applied field. Such a system would be dynamically unstable. Further, as pointed out by Compton and Rognley, the magnetic properties of a substance are vitally affected by temperature, chemical combination and modification of the crystal structure as in the case of the Heusler alloys. On the other hand we cannot, by the most drastic of physical or chemical means, affect the radiation from radioactive substances, thus indicating that the nucleus is not influenced by external conditions. Thus while the results of this experiment are compatable with the theory of Honda, auxiliary evidence seems to indicate that the nucleus cannot be the ultimate magnet.

Ehrenfest has attempted to identify the ultimate magnet with an electron moving within a fixed orbit. In the absence of a magnetic field either sense of revolution is equally probable, while the application of an external magnetic field increases the probability that the sense of revolution of the electron will be such as to produce a magnetic moment in the direction of the field. When one tries to picture the process of magnetization, he is forced to imagine the orbits as turning suddenly, or the electron as suddenly reversing its direction in the orbit. If the whole orbit is able to turn it is difficult to conceive of it as a fixed orbit. If one is to account for hysteresis, energy must be dissipated when the probability of orientation in different directions changes. It then becomes difficult to see how hysteresis can be greatly reduced when the change in direction of magnetization is effected by means of a rotating magnetic field instead of an alternating field.

The Spinning Electron as the Ultimate Magnet

The results of other investigators indicate that neither minute crystal aggregations nor the chemical molecule nor the Rutherford type of atom as a whole can account for ferromagnetism. This experiment shows that it is highly improbable that electrons revolving in any of the orbits are responsible for ferromagnetism. Auxiliary evidence is against the conclusion that the nucleus may account for magnetic properties. It therefore appears that the ultimate magnetic particle should be identified with the spinning electron, as was long ago suggested by Parson[6]; and in accord with Uhlenbeck and Goudsmit's[7] hypothesis of the origin of certain spectroscopic phenomena.

The author wishes to thank Professor A. H. Comptom for proposing the problem, and Dr. R. D. Bennett for constructive suggestions during the course of the experimental work. The kind cooperation of Dr. T. Y. Yensen of the Westinghouse Electric and Manufacturing Company, Professor L. W. McKeehan of Yale University, and Mr. Norman Goss of the American steel and Wire Company in supplying large crystals of iron and silicon steel has made the completion of the work possible.

[5] Honda, "Theory of Magnetism," p. 192.

[6] A. L. Parson, Smithsonian Misc. Collections, Nov., 1915.

[7] Goudsmit and Uhlenbeck, Nature **117**, 264 (1926).

THE FORM OF THE X-RAY DIFFRACTION BANDS FOR REGULAR CRYSTALS OF COLLOIDAL SIZE*

By Carleton C. Murdock
Cornell University

(Received October 23, 1929)

Abstract

The form of the diffraction bands of a very fine uniform crystalline powder has been computed for the (1, 0, 0), the (1, 1, 0) and the (1, 1, 1) planes for cubical and octahedral crystals of the regular system. The shape of the bands is approximately that of the Gauss error curve. Both the shape and the half intensity breadth vary from band to band and the variations are characteristic of the shape of the crystals. There is definite correlation between the form of the band and the direction of the corresponding Bragg planes with respect to the external features of the crystal. The mean breadth of the bands is nearly the same for cubical and octahedral crystals having the same volume. The values of the constant of Scherrer's equation are in general smaller than those computed by other investigators for the cubical case.

Secondary maxima.—A case is found in which secondary maxima of the intensity function would be sufficiently intense to be directly observable. It is pointed out that such an effect might lead to a false interpretation of the crystal structure of a very fine crystalline powder.

WHEN monochromatic x-rays are diffracted by a fine crystalline powder the diffraction bands are found to have a measurable width which is a function of the fineness of the powder. The effect is closely analogous to the low resolving power of a diffraction grating having a small number of lines. In this case we can regard the crystals as three dimensional gratings, the shape and size of which influence the form of the observed diffraction band. Scherrer[1] investigated the case of crystals of the regular (cubic) crystallographic system which are cubical in shape and gave for the half intensity breadth, B, of a diffraction band produced by the powder method,

$$B = \frac{K\lambda}{D \cos(\theta_0/2)} \tag{1}$$

in which λ is the wave-length of the incident x-rays, D, the length of one edge of the cube, and θ_0, the angle between the diffracted and the incident ray. K is a constant whose value Scherrer found to be $2\,[\log 2/\pi]^{1/2}$. Two other investigators treating more general cases have obtained results which reduce to Eq. (1) for the case of cubical crystals. They obtained slightly different values of the coefficient K. Seljakow[2] investigated the case of crystals of any

* This investigation was supported by a grant from the Heckscher Foundation for the Advancement of Research at Cornell University.

[1] P. Scherrer, Nachr. Gesell. Wiss. Göttingen (1918), p. 190.

[2] N. Seljakow, Zeits. f. Physik **31**, 439 (1925).

crystallographic system whose shape is a parallelopiped geometrically similar to the unit cell and whose edges are parallel to the crystallographic axes. v. Laue[3] treated the case of parallelopipeds which have edges parallel to the crystallographic axes but which are not necessarily similar to the unit cell. His development brought out two interesting facts; viz. that the breadth of the diffraction bands depends upon the shape as well as upon the size of the parallelopiped; and in the general case, that the breadth is a function of the Miller indices of the band.

Considerable use has been made of Scherrer's equation in estimating the size of crystalline powders. Particular interest attaches to the investigation of colloidal preparations of such elements as gold, silver and nickel. These elements crystallize in face-centered cubic lattices and are normally of the octahedral form. In the investigations cited above no attempt has been made to determine the shape of the diffraction band. The shape of the band should depend upon the Miller indices of the band, the shape of the crystals, and, if the crystals are not of uniform size, upon the distribution of size. It seemed desirable to investigate the theoretical breadth and shape of several diffraction bands for crystals of octahedral as well as cubical shape.

The general procedure for computations of this sort is given by v. Laue[3] and in the following discussion his notation is generally followed. Assume a parallel beam of monochromatic x-rays incident upon a crystal in a direction which we shall specify by the unit vector $\mathbf{s}_0$. Consider the rays diffracted by the crystal in the direction of the unit vector $\mathbf{s}$. The intensity of the diffracted beam may be expressed[4] as a periodic function of the quantities A_i defined by $A_i = k\ \mathbf{a}_i \cdot \mathbf{H}$; $i = 1, 2, 3$ in which $k = 2\pi/\lambda$ and $\mathbf{H} = \mathbf{s} - \mathbf{s}_0$. $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ represent the three primitive vectors of the space lattice. In the case of fine powders the extinction effect is negligible[5] and each unit cell of the crystal may be regarded as diffracting in the direction of $\mathbf{s}$ rays which are identical except for phase. In the expression for the total intensity of the diffracted beam, A_1, A_2, and A_3 represent the phase differences between rays diffracted by cells adjacent respectively along the three crystallographic axes of the crystal. The principal maxima of the function occur when the phase differences, A_i, are integral multiples of 2π, i.e. when $A_i = 2\pi h_i$; $i = 1, 2, 3$ in which the quantities h_i are integers. It will be noted that h_1, h_2, and h_3 are respectively n times the Miller indices of the Bragg planes of the crystal where n is the order number.

In the cubic system, the magnitudes of the three vectors $\mathbf{a}_i$ are equal and we can write $|\mathbf{a}_i| = a$. This makes it possible to regard A_1, A_2, and A_3 as the projections on the three crystallographic axes of a vector, $\mathbf{A} = ka\mathbf{H}$. Consider a rectangular cartesian system in which A_1, A_2, and A_3 are the coordinates with axes parallel to the crystallographic axes of the crystal. We will designate the space thus defined as A-space. Each point, A_i, of this space deter-

[3] M. v. Laue, Zeits. f. Krist. **64,** 115 (1926).

[4] M. v. Laue, Enc. Math. Wiss. **5,** 459.

[5] R. J. Havighurst, Phys. Rev. [2] **28,** 882 (1926).

mines a value of the intensity function. The points $2\pi h_i$ in A-space form a lattice which is geometrically similar to Ewald's reciprocal lattice.[6] Each such point corresponds to a principal maximum of the diffraction pattern.

Since $\boldsymbol{H}$ is the difference of two unit vectors, $\boldsymbol{s}$ and $\boldsymbol{s}_0$, its numerical value is $2\sin(\theta/2)$ in which θ is the angle between the two vectors, $\boldsymbol{s}$ and $\boldsymbol{s}_0$, i.e. the angle of diffraction. It follows that A, the numerical value of $\boldsymbol{A}$, may be expressed by

$$A = ka\,|\,\boldsymbol{H}\,| = (4\pi a/\lambda)\sin(\theta/2). \tag{2}$$

The direction of $\boldsymbol{A}$ is that of $\boldsymbol{H}$ and depends only upon the directions of the incident and diffracted rays. The vector $\boldsymbol{A}$ is therefore independent of the size, shape and orientation of the crystal. If the incident beam falls upon a crystalline powder, the same vector $\boldsymbol{A}$ pertains to the ray diffracted by each crystal in the direction determined by the angle θ. To each crystal of the powder there corresponds an A-space with axes parallel to the crystallographic axes of the crystal. The total intensity of the beam diffracted through the angle θ by the powder is the sum of the values of the intensities determined in the A-spaces of the several crystals by the vector, $\boldsymbol{A}$.

The intensity function is determined by the size and shape of the crystal, the crystal lattice and the structure factor. Consider a large number, N, of crystals of uniform size, shape, space lattice and structure. Then the same intensity function, J, will pertain to the A-spaces of all the crystals and the total intensity will be found by integrating J between such limits as to include all possible orientations of the crystallographic axes. For the purpose of carrying out this integration, it is convenient to specify the orientation in terms of the direction of $\boldsymbol{A}_0$, the radius vector of the point $2\pi h_i$ in A-space corresponding to the diffraction maximum, h_i, with which we are concerned. Let ϕ be the polar angle between the directions of $\boldsymbol{A}$ and $\boldsymbol{A}_0$; ξ, the azimuth angle about the direction of $\boldsymbol{A}$ as a pole; and ψ, that about the direction of $\boldsymbol{A}_0$ as a pole. The total intensity, I, will then be represented by

$$I = N\frac{\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} J(A_i)\sin\phi\, d\phi d\xi d\psi}{\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}\sin\phi\, d\phi d\xi d\psi}$$

$$= \frac{N}{4\pi}\int_0^{\pi}\int_0^{2\pi} J(A_i)\sin\phi\, d\phi d\psi \tag{3}$$

since $J(A_i)$ is invariant with respect to ξ. This double integral is the same as that representing the integral over the surface of the sphere in A-space whose center is the origin and whose radius is A. It will be convenient to consider I as this surface integral.

The intensity function[4] for the case of a crystal whose shape is a cube with edges parallel to the crystallographic axes is well known. Expressed in terms

[6] P. P. Ewald, Zeits. f. Krist. **56**, 129 (1921).

of the intensity diffracted by one unit cell per unit solid angle in the specified direction, it is given by

$$J=\frac{\sin^2 \frac{1}{2}MA_1}{\sin^2 \frac{1}{2}A_1}\cdot\frac{\sin^2 \frac{1}{2}MA_2}{\sin^2 \frac{1}{2}A_2}\cdot\frac{\sin^2 \frac{1}{2}MA_3}{\sin^2 \frac{1}{2}A_3} \tag{4}$$

in which M is the number of unit cells along one edge of the cube. The principal maxima of J occur when $A_i=2\pi h_i$ and the value of J at these maxima is $J_0=M^6$. Because of its structure the intensity of the rays diffracted by a unit cell will vary with the direction thus causing the various principal maxima to have different intensities. In a study of the variation of intensity within a diffraction band, we compare the surface integrals over spheres in A-space which comprise a very thin spherical shell and we may neglect the variation of the structure factor with respect to A within this shell. This is accomplished by measuring the intensity function in terms of its maximum value at $A_i=2\pi h_i$ for the band, h_i, under investigation and gives

$$J'=J/J_0. \tag{5}$$

Let us investigate the intensity function for an octahedron consisting of a simple cubic lattice with axes x, y, z along the diagonals of the octahedron and a single diffracting particle at each point of the lattice. Let M be the number of diffracting particles along a diagonal. We will take M to be an odd integer. We will specify the points of the lattice by the coordinate whole numbers n_1, n_2, n_3 measured parallel to the x, y, z axes respectively in terms of the length of the unit cell i.e. $x=n_1a$, $y=n_2a$, $z=n_3a$. The points having a particular value of n_3 form a square parallel to the x, y plane whose diagonals extend from $-(m-|n_3|)$ to $(m-|n_3|)$ in which $m=1/2\,(M-1)$. In this square the points having a particular value of n_2 form a row which extends from $n_1=-n_1''$ to $n_1=n_1''$ in which $n_1''=m-|n_2|-|n_3|$. The resultant of the rays diffracted in the direction of $\mathbf{s}$ by the $(2n_1''+1)$ points comprising the n_2, n_3 row will be in phase with that diffracted in this direction by the central point, 0, n_2, n_3, of the row. The contribution of any point, n_1, n_2, n_3 to this resultant is $\cos(n_1A_1)$ multiplied by the amplitude. Measured in terms of the ray diffracted in the direction of $\mathbf{s}$ by any point, the resultant is $\sum_{-n_1''}^{n_1''}\cos(n_1A_1)$. As we now proceed to combine the resultant rays from the various rows of the n_3 square, we are combining rays having unequal amplitudes whose values are symmetrically distributed about the central row, $0,n_3$. Each component ray has the phase of the central point of its row. The resultant will therefore have the same phase as that of the ray diffracted by the central point 0, 0, n_3 of the n_3 square and will be

$$\sum_{-n_2'}^{n_2'}\left\{\cos(n_2A_2)\sum_{-n_1''}^{n_1''}\cos(n_1A_1)\right\}$$

in which $n_2'=m-|n_3|$. Similarly we may combine the rays from all such squares and obtain P, the resultant amplitude of the ray diffracted by the octahedron in the direction of $\mathbf{s}$.

$$P=\sum_{-m}^{m}\left\{\cos(n_3A_3)\sum_{-n_2'}^{n_2'}\left[\cos(n_2A_2)\sum_{-n_1''}^{n_1''}\cos(n_1A_1)\right]\right\}. \tag{6}$$

Principal maxima of P occur when $A_1=2\pi h_1$, $A_2=2\pi h_2$, $A_3=2\pi h_3$ where h_1, h_2, h_3 are integers. The value of these maxima is $P_0=(4m^3+6m^2+8m+3)/3$ and the intensity function measured in terms of the intensity at a maximum is $J'=P^2/P_0^2$. (7)

An investigation of the variation of P with respect to M shows that if P is expressed in terms of new variables, $u_i=1/2\ M(A_i-2\pi h_i)$, it is approximately independent of M in the neighborhood of the point $2\pi h_i$. If we now write the expression for J_∞', the limit of J' as M approaches the summations of Eq. (6) become definite integrals which may be evaluated. The result of the integration is

$$J_\infty'=6\left\{\frac{(u_1^2-u_2^2)u_3\sin u_3+(u_2^2-u_3^2)u_1\sin u_1+(u_3^2-u_1^2)u_2\sin u_2}{(u_1^2-u_2^2)(u_2^2-u_3^2)(u_3^2-u_1^2)}\right\}. \tag{8}$$

An investigation of Eq. (8) shows that the distribution of the values of J_∞' about the origin of u_i is nearly spherical i.e. J_∞' is approximately a single valued function of $u=(u_1^2+u_2^2+u_3^2)^{1/2}$. For any given value of u, maxima or minima occur if (a) $u_j=u_k=0$, (b) $u_i=u_j$, $u_k=0$, or (c) $u_i=u_j=u_k$. On the sphere in A-space whose radius is u and whose center is $2\pi h_i$ these maxima and minima occur at intersections with diameters parallel respectively to (a) the axes of the space lattice, (b) the diagonals of squares bounding the unit cells, and (c) the diagonals of the unit cells. The values of J_∞' for these three conditions are given by

$$\left.\begin{array}{lll}
\text{(a)} & J_\infty'=\dfrac{6}{u_i^3}(u_i-\sin u_i), & u=u_i \\
(b) & J_\infty'=\dfrac{3}{u_i^3}(\sin u_i-u_i\cos u_i), & u=\sqrt{2}u_i \\
\text{(c)} & J_\infty'=\dfrac{3}{4u_i^3}[(1+u_i^2)\sin u_i-u_i\cos u_i], & u=\sqrt{3}u_i
\end{array}\right\} \tag{9}$$

and are shown as functions of u in curves Ia, Ib, and Ic of Fig. 1. For values of $u>5.7$, minima at which $J_\infty'=0$ occur at other points on the sphere. It follows that when $u<5.7$ all values of J_∞' must lie in the narrow strip enclosed between the curves and when $u>5.7$, in that enclosed between the curves and the line $J_\infty'=0$.

The nature of the approximation involved in using Eq. (8) instead of Eq. (7) is shown by curves Ia, Ib and Ic of Fig. 2. Here the corrections which must be applied to J_∞' in order to obtain the value of J' for the case, $M=11$ are plotted against u. The correction curves for larger values of M are of the same general form with maxima and minima approximately at the same values of u, but they have smaller values for the ordinates. The correction for any

value of u is approximately inversely proportional to M^2. For values of M which ordinarily occur these corrections are small.

The secondary maxima of the function J' defined by Eqs. (6) and (7), lie on the diagonals of the cubes of the lattice formed in A-space by the principal maxima points, $2\pi h_i$. At the centers of these cubes where three such diagonals intersect there occur secondary maxima at which the intensity is approximately three times that at the neighboring secondary maxima. The large ordinate at $u = 29.9$ in curve Ic of Fig. 2 is due to such a large secondary maximum. In the derivation of Eq. (6), M was assumed to be odd. If M were even, no secondary maxima would occur at these points in A-space.

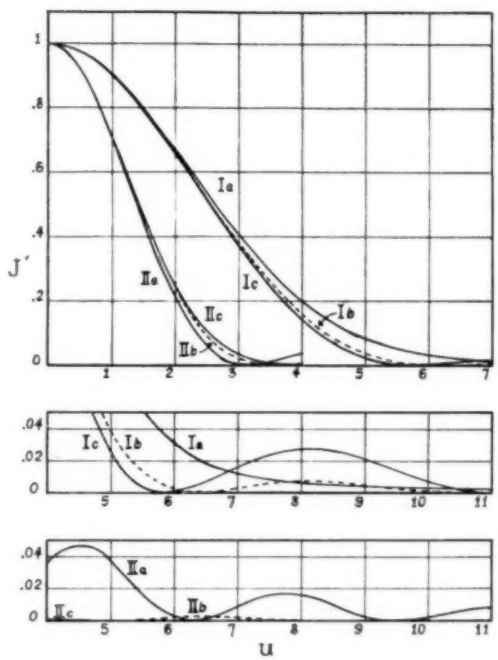

Fig. 1. The intensity function, J_m', plotted against u; (I), for octahedral crystals; (II), for cubical crystals. u is measured parallel to the radius vector $\boldsymbol{A}_0$ of (a) the (1, 0, 0) maximum, (b) the (1, 1, 0) maximum, (c) the (1, 1, 1) maximum.

Substituting the coordinates of these points, $(2\pi h_i - \pi)$, for A_i in Eq. (6) we obtain $P = (-1)^m (3/M)\ (M^2+1)\ /(M^2+5)$ which gives a value of J approximately $9/M^2$ times that at the neighboring principal maxima. Colloidal crystals have been examined by x-rays[7] for which the equivalent value of M was as small as 9. Crystals of this size, having octahedral shape and a simple cubic lattice would form an x-ray powder spectrogram in which these large secondary maxima should be directly observable as faint diffraction bands. The principal maxima points, $2\pi h_i$, form in A-space a simple cubic lattice, geometrically similar to the reciprocal lattice[8] of the crystal. If we include the large secondary maxima points, $(2\pi h_i - \pi)$, the reciprocal lattice becomes body-centered. Since the reciprocal lattice of a face-centered crystal is a body-

centered lattice, the observed diffraction pattern would be similar to that of a face-centered crystal. The relative strengths of the bands would be very much like that observed in the diffraction pattern of sodium fluoride.

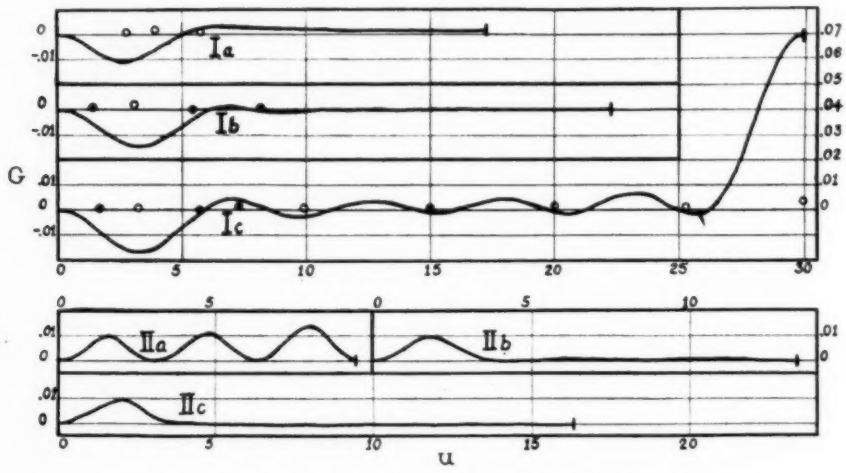

Fig. 2. The correction function, $G(M, u_i) = J' - J_\infty'$ plotted against u; for a simple cubic lattice; (I) octahedral crystals, $M = 11$; (II) cubical crystals, $M = 6$. The small circles show corresponding values for a face-centered lattice. u is measured parallel to the radius vector A_o of (a) the (1, 0, 0) maximum, (b) the (1, 1, 0) maximum, (c) the (1, 1, 1) maximum.

The intensity function in the case of a cubical crystal may be treated in the same way as in the case of an octahedral cystal. If we express J' of Eq. (5) in terms of u_i and take the limit as M approaches ∞ we obtain

$$J_\infty' = \frac{\sin^2 u_1}{u_1^2} \cdot \frac{\sin^2 u_2}{u_2^2} \cdot \frac{\sin^2 u_3}{u_3^2}. \tag{10}$$

The conditions for maxima and minima of this function are similar to those for Eq. (8). Curves IIa, IIb, and IIc of Fig. 1 show the corresponding maxima and minima as functions of u. In this case additional minima at which $J_\infty' = 0$ occur for values of $u > 3.3$. Curves IIa, IIb, and IIc of Fig. 2 show the corrections to be added to J_∞' to obtain the value of J' for the case, $M = 6$. Here also the correction for a particular value of u is inversely proportional to M^2.

Since crystals having face-centered lattices are of particular interest, the intensity functions have been developed also for diffracting particles at the points of a face-centered lattice. In the octahedral case, the result is

$$J' = \left[\frac{P+Q}{P_0+Q_0}\right]^2 \tag{11}$$

in which

$$Q = \sum_{-m+1}^{m-1} \left\{ \cos\ (n_3 A_3)\ 4 \sum_{0}^{n_2'-1} \left[\cos\ (n_2 A_2 + \tfrac{1}{2} A_2)\ \sum_{0}^{n_1''} \cos\ (n_1 A_1 + \tfrac{1}{2} A_1) \right] \right\}$$

[7] R. Zsigmondy, "Kolloidchemie," Leipzig 1920, p. 406.

[8] cf. A. L. Patterson, Zeits. f. Physik **44**, 596 (1927).

+two other terms formed from the first by a rotation of subscripts and $Q_0 = 4m^3+6m^2+2m$. The limit of J' as M approaches ∞ is identical with J_∞' as given by Eq. (8). The corrections to be added to J_∞' to obtain J' are so small that the curves have not been drawn. The points indicated by the small circles in Fig. 2 indicate some of the values for $M=11$.

In the case of crystals of cubical shape with a face-centered lattice

$$J' = \left(\frac{R+S}{R_0+S_0}\right)^2 \tag{12}$$

in which $R = J^{1/2}$ as given by Eq. (4), $R_0 = M^3$,

$$S = \frac{\sin \frac{1}{2}MA_1}{\sin \frac{1}{2}A_1} \cdot \frac{\sin \frac{1}{2}(M-1)A_2}{\sin \frac{1}{2}A_2} \cdot \frac{\sin \frac{1}{2}(M-1)A_3}{\sin \frac{1}{2}A_3}$$

+ two other terms formed from the first by rotation of subscripts and $S_0 = 3M(M-1)^2$. The limit of J' as M approaches ∞ is identical with J_∞' as given by Eq. (10). The corrections to be added to J_∞' to obtain J' are larger than in

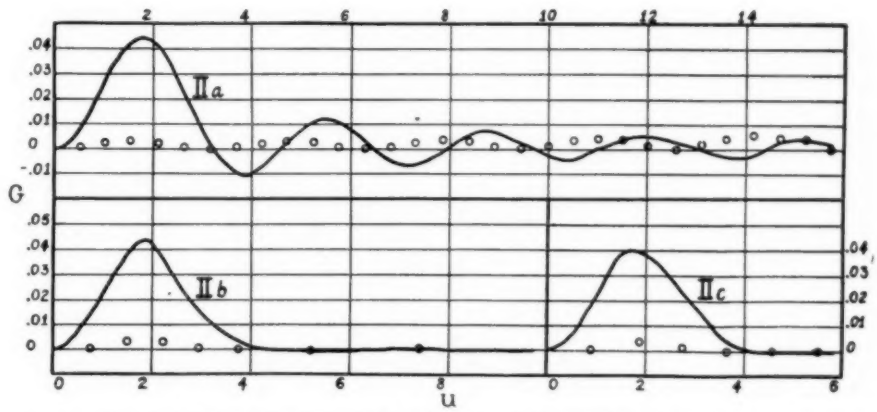

Fig. 3. The correction function, $G(M, u_i) = J' - J_\infty'$ plotted against u for a face-centered lattice and cubic crystals, $M=10$. The small circles show corresponding values for a simple cubic lattice. u is measured parallel to the radius vector $\boldsymbol{A}_0$ of (a) the (1, 0, 0) maximum, (b) the (1, 1, 0) maximum, (c) the (1, 1, 1) maximum.

the other cases studied. The curves are shown in Fig. 3 for $M=10$. As in the other cases the positions of the maxima of these curves vary but slightly with M. In this case the ordinates are approximately inversely proportional to M. For the purpose of comparison, corrections for the case of the cubical shape with a simple cubic lattice for $M=10$ are shown in Fig. 3 by small circles.

The narrow limits, between which all values of the intensity function must lie as shown in Fig. 1, make it possible to select an integrable function of u which closely approximates J. An approximate solution of our problem may be obtained by substituting this function for J in Eq. (3) and performing the integration. An investigation[9] of the case of octahedral crystals by this

[9] C. C. Murdock, Phys. Rev. [2] **31**, 304 (1928).

method gave the value of the constant K of Eq. (1) as 1.6 when D was measured through the center of the octahedron from corner to corner. The investigation showed that the value of K was different for the various diffraction bands. The method of procedure, however, is not suitable for the study of this variation or for the determination of the form of a diffraction band.

Let us represent the function, J_∞', by the expression, $e^{-u^2/p^2}+F(u_i)$ in which the value of p is so selected that the first term approximates J_∞' for the case under consideration. We may now express J of Eq. (3) as

$$J=J_0J'=J_0\{J_\infty'+G(M,u_i)\}=J_0\{e^{-u^2/p^2}+F(u_i)+G(M,u_i)\} \qquad (13)$$

in which $G(M,u_i)$ represents the correction to be added to J_∞' in order to obtain J'. The ordinates of Figs. 2 and 3 are values of G for the particular cases shown. We will use u^2 in place of ϕ as the variable of integration.

$$\begin{aligned} u^2&=u_1^2+u_2^2+u_3^2\\ &=\tfrac{1}{4}M^2[A^2+4\pi^2h^2-4\pi(h_1A_1+h_2A_2+h_3A_3)]\\ &=\tfrac{1}{4}M^2[A^2+4\pi^2h^2-4\pi hA\cos\phi] \end{aligned}$$

in which $h^2=h_1^2+h_2^2+h_3^2$. Therefore $d(u^2)=\pi hAM^2\sin\phi\,d\phi$.

In terms of u^2 the limits of integration of Eq. (3) become v^2 and w^2 where $v=\frac{1}{2}M(A-2\pi h)$ and $w=\frac{1}{2}M(A+2\pi h)$. These limits are such that the integration may be considered as a surface integration over the surface of a sphere in A-space whose diameter is $2A$. In changing variables from A_i to u_i we shifted the origin to the point, $2\pi h_i$, associated with the diffraction band, h_i, with which we are concerned. We also changed the scale of the space by the factor $1/2\,M$. In terms of the new scale, the diameter of the sphere of integration is $AM=w+v$. The diameter of the sphere which passes through the point $2\pi h_i$ is $2\pi hM=w-v$. The point $2\pi h_i$ is not the only point on the surface of this sphere at which a principal maximum of J occurs. For example on the sphere of integration for the (1, 1, 1) diffraction band there are eight points, $2\pi h_i$, corresponding to the following values of h_i; 1, 1, 1; -1, 1, 1; 1, -1, 1; 1, 1, -1; 1, -1, -1; -1, 1, -1; -1, -1, 1; and -1, -1, -1. Let N' represent the number of such points. Since J is a periodic function of A_i, the integration indicated in Eq. (3) includes the values of J in the neighborhood of all these points and the contribution to the integral in the neighborhood of each point is identical. J_∞' is not a periodic function. It can approximate J_0J only in the neighborhood of the point, $2\pi h_i$. In its integration the limits should be fixed so as to include $1/N'$ times the area of the sphere and the integral should be multiplied by N'. It will not be found necessary to specify exactly the upper limit of this integration. Its order of magnitude may be ascertained by taking the upper limit of u^2 as r^2, where r represents the radius of a circle whose area is $1/N'$ times the area of the sphere. Thus $\pi r^2=4\pi^3h^2M^2/N'$ and $r^2=4\pi^2M^2h^2/N'$. The value of h^2/N' is 1/6 for the (1, 0, 0) and the (1, 1, 0) diffraction bands, but has a larger value for each of the other bands. The upper limit of integration is therefore of the order of magnitude of $2/3\,\pi^2M^2$ or larger.

Making these substitutions in Eq. (3) we obtain

$$I=\frac{NN'J_0}{4\pi^2hAM^2}\left[\int_{v^2}^{r^2}e^{-u^2/p^2}d(u^2)+\int_{v^2}^{r^2}f(u,v)d(u^2)+\int_{v^2}^{r^2}g(M,u,v)d(u^2)\right]$$

$$=\frac{NN'J_0}{4\pi^2hAM^2}[U+V+W], \tag{14}$$

in which $f(u,v)=1/2\pi\int_0^{2\pi}F(u_i)\,d\psi$, the average value of F with respect to ψ, $g(M,u,v)=1/2\pi\int_0^{2\pi}G(M,u_i)\,d\psi$ and U, V, and W represent respectively the three integrals of the equation.

The first integral, U, of Eq. (14) has the same value for each band, h_i, and may be written

$$U=\int_{v^2}^{r^2}e^{-u^2/p^2}d(u^2)=p^2e^{-v^2/p^2} \tag{15}$$

if r^2/p^2 is large. Since $r^2/p^2\geqq\frac{2}{3}\pi^2M^2/p^2$ and M^2/p^2 is of the order of 10 for the smallest colloidal crystals so far studied,[7] this assumption is justified.

The second integral, V, of Eq. (14) varies from band to band. It may be evaluated graphically by the following method. Contour plots are made of the function, $F(u_i)=J_\infty{}'-e^{-u^2/p^2}$ for a number of values of u. These may be made on the surfaces of spheres, the radii of which are taken as equal to u. It has been found more convenient, however, to make plots which are the projections of such spherical plots upon planes tangent to the sphere and perpendicular to the direction of the vector $\boldsymbol{A}_0$. From these plots the curves for $F(u_i)$ at various values of u and v are plotted as functions of ψ and integrated by inspection to obtain the values of $f(u,v)$. These values are then plotted as functions of u^2 for various values of v and the integrals evaluated graphically.

It is not practicable to carry out this process to the upper limit of integration. For large values of u, the value of f becomes small but remains finite and small errors in the function produce large errors in the integral due to the fact that the integration is performed with respect to the square of u. If s^2 is the upper limit of the graphical integration it leaves a part, $\int_{s^2}^{r^2}f(u,v)d(u^2)$, unevaluated. By properly choosing the value of s, the error involved in neglecting this part of the integral may be compensated in making the experimental observations. In an experiment the incident radiation will not be strictly monochromatic. Moreover there will be some generally scattered radiation. Both of these effects will give a background intensity superimposed upon that which we are computing. In practice the intensity is measured on either side of a diffraction band and from these data the background intensity is estimated for the points in the band on the assumption that there are no maxima or minima in the background intensity in that region. If the value of s is taken two or three times the largest value of v used, this assumption is also justified for $\int_{s^2}^{r^2}f(u,v)\,d(u^2)$ and the part of the intensity proportional to it will be automatically subtracted from the measured intensity as part of the background correction.

The third integral, W, of Eq. (14) may be evaluated by the method used for the evaluation of V. If, however, G can be approximated by an integrable function of u, it will be simpler to proceed as in the case of J_∞'. An examination of the correction curves of Figs. 2 and 3 shows that the (a), (b) and (c) curves of each set are practically identical for the smaller values of u and that for the larger values, two curves of each set have small ordinates. Advantage may be taken of this to approximate G by the function $Cu^2e^{-u^2/p^2}$ which gives as a first approximation

$$W = Cp^2(p^2+v^2)e^{-v^2/p^2}. \tag{16}$$

C is a function of M. It may be expressed for the various cases studied as shown in Table I.

TABLE I.

	Cube	Octahedron
Simple lattice	$C=1/(3M^2)$	$C=-1/(2M^2)$
Face-centered lattice	$C=1/(3M)$	$C=0$

The remainder, $G-Cu^2e^{-u^2/p^2}$, may now be integrated by the method described for the evaluation of V.

Since W depends upon M, which, in general, can only be known as a result of the solution of our problem, we will first investigate the case in which W is negligible. If $W=0$, Eq. (14) may be written

$$I = \frac{NN'J_0L}{4\pi^2hAM^2}, \tag{17}$$

in which $L=U+V$. L is the surface integral over the sphere of $N'J_\infty'$. The only quantities in the second member of Eq. (17) which depend upon v, are L and A. If, therefore, we measure the intensity in terms of its maximum value, I_0, for which $v=0$, we obtain

$$I' = I/I_0 = L'A_0/A, \tag{18}$$

in which $L'=L/L_0$ and L_0 represents the value of L when $v=0$. The factor A_0/A may be written by Eq. (2) as $\sin(\theta_0/2) \div \sin(\theta/2)$ in which θ_0 is the value of θ corresponding to the maximum, h_i. In this form it is seen to be determined by directly observable quantities. Within a diffraction band θ differs only slightly from θ_0 and the factor may be written $1/(1+\frac{1}{2}\cot(\theta_0/2)\,\Delta\theta)$ where $\Delta\theta=\theta-\theta_0$. Since this factor is unsymmetrical with respect to $\Delta\theta$ it introduces asymmetry in the diffraction band. It is due to the fact that the integrations for values of v which are numerically equal but of opposite sign, are performed over spheres of different areas. In the graphical process for the evaluation of V another source of asymmetry occurs. It is due to the curvature of the spherical surface. No case has yet been found in which this second asymmetry is large enough to be taken into consideration. Because of the small value of

s used in the evaluation of V an integration in the spherical surface is practically the same as an integration in the tangent plane perpendicular to the vector, $\boldsymbol{A}_0$. If the integration is performed in this plane, the asymmetry due to curvature does not appear in the result.

We may now write Eq. (18) as

$$L' = [1+\tfrac{1}{2}\cot(\theta_0/2)\Delta\theta]\, I'. \tag{19}$$

In this form there are collected in the second member the experimentally observable factors and the first member is a symmetrical function which may be computed for any band h_i from the integrals U and V of Eq. (14). U is the same for all bands. If V is integrated over the tangent plane it will vary from band to band due to the variation of the direction of the vector $\boldsymbol{A}_0$. This is, however, the same for all bands having the same Miller indices. It follows that the function L' will be the same for all orders of a diffraction band and need only be computed for one order.

The function L' has been computed for the (1, 0, 0), the (1, 1, 0), and the (1, 1, 1) diffraction bands in the cases of cubical and octahedral crystals. In the cubical case, the value of p was taken as $\sqrt{3}$, contour plots were made for eight values of u, and the graphical integration performed to the limit $s^2 = 90$. In the octahedral case the value of p was taken as 3, contour plots were made for eleven values of u, and the graphical integration performed to the limit $s^2 = 120$. Table II gives the resulting values of L' as determined. The uncertainty in the values due to the errors of the operation are of the order of ± 0.005. Since L' is a symmetrical function the values are given for the positive values of v only.

TABLE II.

v	Cube L' (1, 0, 0)	(1, 1, 0)	(1, 1, 1)	v	Octahedron L' (1, 0, 0)	(1, 1, 0)	(1, 1, 1)
0	1.000	1.000	1.000	0	1.000	1.000	1.000
1	.728	.692	.680	1	.874	.891	.905
1.41	.500	.445	.466	2	.591	.631	.673
1.73	.333	.300	.333	2.6	.428	.456	.504
2	.221	.211	.268	3.2	.292	.305	.348
2.5	.074	.123	.170	4	.177	.145	.170
3	.027	.089	.131	5	.105	.060	.051
3.5			.094	6	.064	.046	.020
4	.054	.072	.069	7	.039	.040	.025

Experimentally we measure the width of a diffraction band in terms of differences in the angle of diffraction. By the definition of v, and by Eq. (2), we obtain

$$v = \tfrac{1}{2}M(A - 2\pi h) = (2\pi a M/\lambda)[\sin(\theta/2) - \sin(\theta_0/2)].$$

If we substitute $d/d\theta\,(\sin\theta/2)\,\Delta\theta$ for $\sin(\theta/2) - \sin(\theta_0/2)$ we obtain

$$v = (\pi a M/\lambda)\cos(\theta_0/2)\Delta\theta.$$

Let v' represent the value of v for which $I' = 1/2$ and, following Scherrer, let B represent the half intensity breadth of a diffraction band, measured in radians. Then

$$v' = (\pi a M/\lambda) \cos(\theta_0/2)\,(B/2)$$

and

$$B = (2v'/\pi)\cdot\lambda/(Ma\cos(\theta_0/2)). \tag{20}$$

This is identical with Eq. (1) obtained by Scherrer since $Ma = D$, the length of the crystal along a crystallographic axis. Thus we obtain for the value of K, $2v'/\pi$. For comparing crystals of different shape, it is convenient to measure the size of the crystal in terms of D', the cube root of the volume. D' may be used in place of D in Scherrer's equation, if a suitably modified constant K' is used in place of K. For the cubical shape $D' = D$ and $K' = K$. For the octahedral shape $D'^3 = 1/6\ D^3$ and $K' = K/6^{1/3}$ Table III shows the values of v', K and K' as computed from the data of Table II.

TABLE III.

Indices	Cube		Octahedron		
	v'	$K = K'$	v'	K	K'
(1, 0, 0)	1.41	0.90	2.32	1.48	0.81
(1, 1, 0)	1.32	0.84	2.45	1.56	0.86
(1, 1, 1)	1.36	0.87	2.62	1.67	0.92

These values are in general smaller than the results of previous investigations. Scherrer's value of K as computed from Eq. (1) is 0.94. Seljakow[2] obtained 0.92 and v. Laue[3] 0.90 for the value of K for the cubical case. The previous investigation[9] of the octahedral case gave $K = 1.6$ or $K' = 0.88$, a value 7 percent less than Scherrer's value of K. This difference was attributed to the shape of the crystal and it was concluded that the values of the crystal volumes which have been estimated by the use of Scherrer's equation were too large by 20 percent if the true shape of the crystals was octahedral. It now appears that the smaller value of K was due not so much to the shape of the crystals as to the method of computation. An examination of Table III shows that the mean values of K' in the cubical case and in the octahedral case are practically the same. Both Seljakow[2] and v. Laue[3] used methods which may be regarded as the substitution of a function of u for the intensity function.

The results shown in Table III illustrate the dependence of the half intensity width of a diffraction band upon the indices of the band. The numerical order of the values of K in the two cases is different. In the cubical case the largest value of K is that of the (1, 0, 0) band while in the octahedral case it is that of the (1, 1, 1) band. In each case, the value of K for the diffraction band which is associated with a Bragg plane, parallel to a face of the crystal, is larger than the values which are associated with the other planes.

The shape of the crystals not only influences the relative width of the diffraction bands but also the form of the bands. This is shown in Fig. 4 in which

L' is plotted against v/v', or what is the same thing, $2\Delta\theta/B$. On this scale the half intensity width of all the diffraction bands is 2 and their shapes can be directly compared.

The upper halves of all the curves are practically the same and are sufficiently approximated by the exponential relation $L' = e^{-(v/1.2v')^2}$ which is

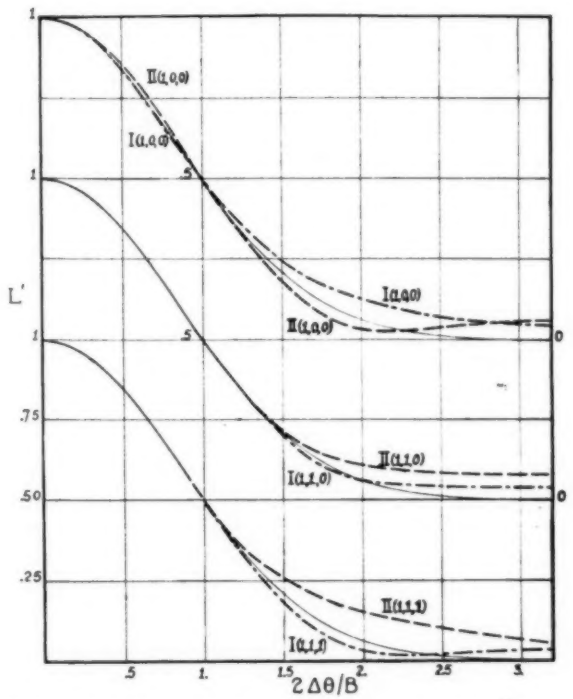

Fig. 4. The (1, 0, 0) (n), the (1, 1, 0) (n) and the (1, 1, 1) (n) diffraction bands for, (I) octahedral crystals, (II) cubical crystals. The scales are such that the maximum intensity is 1 and the half intensity breadth is 2. The unbroken line shows the corresponding Gauss error curve.

plotted in unbroken lines in the figure. The lower halves of the curves show marked variations. Three types occur:

(a) that illustrated by I(1, 1, 1) and II(1, 0, 0), falls slightly below the exponential curve to a minimum and then rises to a secondary maximum;

(b) that illustrated by I(1, 1, 0) and II(1, 1, 0) follows the exponential curve until well below the half intensity point and then becomes nearly parallel to the v/v' axis;

(c) that illustrated by I(1, 0, 0) and II(1, 1, 1) lies well above the exponential curve throughout the lower half of the curve and continues to approach the axis of v/v' to the limits of the computation.

There is a correlation between the type of curve and the Bragg plane associated with the diffraction band. Type (a) occurs when the Bragg plane is parallel to the faces of the crystal, the (1, 0, 0) for the cube and the (1, 1, 1) for the octahedron. These are the same bands which show large values of K.

Type (c) occurs when the Bragg planes are perpendicular to lines connecting opposite corners of the crystal, the (1, 1, 1) for the cube and the (1, 0, 0) for the octahedron. Type (b) occurs for the (1, 1, 0) band in both cases. In both the cube and the octahedron the (1, 1, 0) planes are perpendicular to lines connecting the centers of opposite edges of the crystal. The extension of this correlation to the case of crystals of dodecahedral shape would suggest that in this case the (1, 1, 0) diffraction band would be of type (a).

These results have been obtained by assuming that the third integral, W, of Eq. (14) was negligible. This will not be true if M is very small. By Eq. (20) and Table II we may now estimate the value of M and compute corrections to account for the finite value of W. If $W \neq 0$, we must write in place of L' of Eqs. (18) and (19), $(L+W)/(L_0+W_0)$ in which W_0 is the value of W when $v=0$.

If W is small compared with L_0 we may write $(L+W)/(L_0+W_0) = L' + (W/L_0) - (W_0/L_0)\ L'$ and compute W by Eq. (16) taking $p^2 = (1.2v')^2 = L_0$. This gives for the correction to be applied to L',

$$\Delta L' = W/L_0 - (W_0/L_0)L' = Cv'^2\left\{(v/v')^2 e^{-v^2/p^2} - 1.2^2(L' - e^{-v^2/p^2})\right\}. \qquad (21)$$

This may be readily computed. C is given in Table I; v' in Table II; v/v' are the abscissa of Fig. 4; and e^{-v^2/p^2} are the corresponding ordinates of the unbroken line curves of Fig. 4.

At the half intensity point, Eq. (21) reduces to $\Delta L' = \frac{1}{2}Cv'^2$. If we assume the slope at the half intensity point to be that of the unbroken line curve we obtain for the correction to be applied to v',

$$\Delta v' = 0.72Cv'^3. \qquad (22)$$

Thus v' may be corrected for the finite value of W by multiplying it by the factor $(1+0.72\ Cv'^2) = (1+1.8\ CK^2)$. Since K and K' are proportional to v' this same correction factor may be applied to them and also to the values of D and M as computed by Scherrer's equation.

Eqs. (8) and (10) have been derived for the face-centered, as well as for the simple lattice. They may be shown to hold for the body-centered lattice as well. It follows that J', its integral, L, and the results shown in Tables II and III and Fig. (4) hold for any of these space lattices. However, the corrections to these results computed by Eqs. (21) and (22) vary with the space lattice. The corrections have been derived on the assumption that the diffracting material is concentrated at the points of the lattice. Actually these points are merely centers of space distributions of diffracting material. Since the corrections depend upon the distribution of diffracting material within the unit cell, a more exact determination of W than that given by Eq. (16) does not seem to be warranted by the assumptions.

It has been assumed throughout the discussion that the crystalline powder is made up of crystals of uniform size. In practice this assumption is frequently not justified. Any attempt to determine the size distribution from the x-ray diffraction pattern requires a knowledge of the theoretical form of

the band for the case of uniform size. Indeed it was this requirement which instigated this investigation. The closeness with which the form of the diffraction bands agrees with the Gauss error curve as shown in Fig. 4 makes it possible to assume this form for the purpose of estimating the distribution of particle size. The (1, 1, 0) band is particularly suitable for this purpose. It is hoped that studies of the form of the (1, 0, 0) and (1, 1, 1) bands together with studies of the relative width of the bands will lead to information as to the shape of the colloidal crystals in cases where there is approximate uniformity of shape.

The shape of the x-ray diffraction bands of a very fine uniform crystalline powder has been computed for the (1, 0, 0), (1, 1, 0) and (1, 1, 1) planes of cubical and octahedral crystals of the regular system. The results are shown in Fig. 4 plotted to such scales that the maximum ordinate is 1 and the half intensity breadth, 2. The coefficient K of Eq. (1) which relates the half intensity breadth of a band to the size of the crystal has been computed for each case. The values are shown in Table III. In comparing these theoretical results with experimental data, one must take care to comply with the following conditions.

(a) The experimental data must be corrected for "background" radiation and instrumental errors.

(b) The corrected data must be multiplied by the asymmetrical factor, $[1+\frac{1}{2}\cot(\theta_0/2)\,\Delta\theta]$ of Eq. (19).

(c) An approximate value of M should be computed by Eq. (20) and Table III.

(d) The corrections to the ordinates of Fig. 4 may then be computed by Eq. (21) and Table I and the approximate value of M may be corrected by the factor $(1+1.8\,CK^2)$.

I wish to express my thanks to Sir William Bragg and to the managers of the Royal Institution for putting at my disposal the facilities of the Davy-Faraday Laboratory where the work of this investigation was started. I wish also to acknowledge the valuable assistance of Miss M. A. Ewer who carried out a considerable part of the computations.

SPECTRAL PHENOMENA IN SPARK DISCHARGES

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Abstract

Two methods are described for measuring the differences in the time of appearance of the spectrum lines in sparks. The first is a refinement of the Kerr cell method previously used and a detailed description of its use is included. The criticisms of Gaviola of the method are shown not to apply. The second method makes use of a rapidly rotating mirror which either reflects the dispersed light of the spark to a photographic plate or the undispersed light to the slit of a spectrograph. In either case the position of the beginning of a line on the photographic plate gives its time of appearance. The method of Henriot and Hunguenard was used to rotate the mirror. Photographs of sparks are shown with the mirror rotating 1830 r. p. s. However, higher rotational speeds have been used. It is concluded that the Kerr cell method is superior for examining the air lines in the initial stages of the spark; while the rotating mirror method is better in studying the appearance and duration of the metallic lines which are not present in the very first stages of the spark discharge.

ALTHOUGH the electric spark in air has been the subject of a very large number of careful investigations, most of the mechanisms in the various stages of the discharge still remain obscure. This state of affairs probably results from the fact that the essential phenomena of the spark occur in such a short interval of time that the apparatus used in most cases failed to separate them into their component parts. However, during the last few years considerable progress has been made in the study of the various stages of the spark, due largely to the development of several methods of investigation that make it possible to study processes occurring in from 10^{-6} to 10^{-9} sec. It is the purpose of this paper to describe two independent methods of investigating the spark discharge and to record some of the results obtained.

When the sparking potential is first applied across a spark gap the discharge does not take place instantaneously, but a certain average time is required for the initiation of the discharge.[1] This time—usually called the time lag of the spark—is decreased by increasing the overvoltage and becomes in some cases of the order of magnitude of 10^{-8} sec.[2]

When once the discharge is initiated and the effective resistance across the gap starts falling, very little is definitely known of the process except

[1] Sir J. J. Thomson, Conduction of Electricity Through Gases, Cambridge University Press, 2nd Edition, p. 431.

[2] P. O. Pedersen, Ann. d. Physik **71**, 317 (1923); Rogowski, Archiv f. Electrotech. **16**, 496 (1926); Torok, Jour. A.I.E.E. **47**, 177 (1928); Beams, Jour. Franklin Inst. **206**, 809 (1928); L. B. Loeb, Science **59**, 509 (1929)—Suggests a possible explanation of these short time lags.

that the potential across the gap does not fall instantaneously to zero but decreases at a finite and measurable rate.[3]

If the light emanating from the spark in air during its initial stages is examined spectroscopically, it is found that all the spectrum lines do not appear simultaneously. In general the air lines appear first, followed by the spark lines of the metal with the metallic arc lines appearing last. Observations on these phenomena were first made by Schuster and Hemsalech,[4] while they were studying the duration of lines in metallic sparks. Their method consisted essentially in projecting the spectrum on a rapidly moving photographic film and measuring the relative positions of the various parts of the lines. Other workers[5] have observed the spark in a rotating mirror with similar results. The time resolving power of their methods, however, was not sufficient to give anything but rough qualitative results. Recently[6] a method based upon the findings of Abraham and Lemoine[7] that the Kerr effect in some liquids disappears very quickly after the electric field producing it is relaxed, has been successfully used to measure the order of appearance of spectrum lines in condensed discharges. By this method the values for the differences in the time of appearance of the various air lines themselves as well as the lines of a few metals were measured directly in terms of the velocity of light.[8] Since that time the method has been considerably refined and the observations on the air lines repeated. These values have also been confirmed by a rotating mirror method within the limits of precision of the latter method.

The experimental arrangement, except for refinements and details, is essentially the same as that previously described. The method, however, has been recently questioned[9] on the basis that oscillations of large amplitude should exist that would complicate the results.* Since in the work care was taken to investigate experimentally the magnitude of the oscillations present and, since the writer believes the method might find applications to other experiments, it will be described somewhat more in detail.

In Fig. 1 light from the spark A, made parallel by a lens L, plane polarized by a Nicol prism N_1, passes through a Kerr cell K, made by immersing two parallel metallic plates in CS_2, into a second Nicol prism N_2 crossed with

[3] Lawrence and Beams, Phys. Rev. **32,** 483 (1929).
[4] Schuster and Hemsalech, Phil. Trans. **193A,** 212 (1900).
[5] E. C. C. Baly, Spectroscopy **2,** 153 Longmans (1927).
[6] Brown and Beams, J.O.S.A. **11,** 11 (1925).
[7] Abraham and Lemoine, Comptes Rendus **129,** 206 (1899).
[8] Beams, Phys. Rev. **28,** 475 (1926).
[9] Gaviola, Phys. Rev. **33,** 1023 (1929).

* Note: In the writer's opinion the questions raised by Gaviola (loc. cit.) and by L. V. Hamos [Zeits. f. Physik **52,** 549 (1928)] concerning the "electro-optical shutter" have been adequately investigated and reported [Beams and Lawrence, Jour. Franklin Inst. **206,** 169, (1928)]. The cause of the discrepancy in the values in the difference in the average lags of the Faraday effect as observed by Beams and Allison, [Phys. Rev. **29,** 161 (1927)] and Allison, [Phys. Rev. **30,** 66 (1927)], which Dr. Gaviola claims no attempt was made to explain, was investigated and discussed by Allison in the paper referred to and shown to be due to the effect of wave-length upon the lag.

respect to N_1. If a potential is applied across the plates of K and the plane of polarization of the light makes an angle (45° in these experiments) other than zero or 90° with the lines of force, light can pass N_2 because of the double refraction in K.[10] This double refraction produced in CS_2 by the electric field is called the Kerr effect. If μ_1 and μ_2 are the refractive indices for the

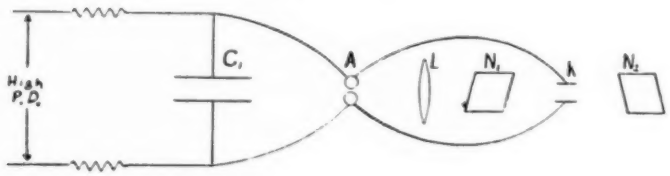


Fig. 1

two rays then their phase difference after passing through the Kerr cell K is $D=2\pi l/\lambda(\mu_1-\mu_2)=2\pi BlE^2$, where λ is the wave-length of the light, B is a constant for a given substance, wave-length and temperature, l is the length of the light path through the liquid, and E is the electric field strength. The intensity of light passing N_2 is

$$I=A\sin^2 D/2=A\sin^2 \pi BlE^2$$

where A is a constant. As a result, for comparatively small values of D (6° to 16°) as used in most of these experiments, the intensity of light passing N_2 varies approximately as the fourth power of the field strength.

If an electric potential is slowly applied across the spark gap A in air until the spark discharge takes place, it has been previously found that no light from the spark intense enough to be detected by the eye passes N_2, provided the lead wires are not too long and are approximately the same length as the light path. The Kerr effect in K therefore effectively vanishes by the time that the light reaches the cell, or the light from the spark is too faint to be observed for a certain time after the beginning of the discharge. If, however, the lead wires from A to K were lengthened, the light path remaining fixed, light passes N_2. When the light was examined spectroscopically it was found that the spectrum lines for any given substance appeared in a definite order which was not a function of their wave-length or of their intensity when measured over the entire duration of the spark.

Fig. 2 shows schematically the arrangement used to measure the time between the appearance of the lines directly in terms of the velocity of light. The arrangement in Fig. 1 is merely modified to allow the light to pass to a movable trihedral mirror system M_1 before entering the cell. The mirror system, designed by Professor L. G. Hoxton, returns a beam of light parallel but displaced. The three mirrors silvered on the front surface are mutually perpendicular and mounted on a steel frame which slides on a wooden track 23 meters in length. The optical system was adjusted (with Nicol prisms uncrossed) until the intensity of the light passing N_2 remained constant while the mirror system was moved throughout the length of its track.

[10] Kerr, Phil. Mag. **1**, 337 (1875); **8**, 85 (1879).

The lead wires from A to K were either symmetrical and equal in length or one of the leads was removed and one side each of A and K grounded with short wires to high capacity grounds as shown in Fig. 2. The lead can be lengthened or shortened over the ranges being investigated by a sliding copper bar T. The inductance and capacity of both the lead wires and K were made as small and uniformly distributed as conveniently possible. In some of the experiments a resistance $R=(L/C)^{\frac{1}{2}}$ (app. 500 ohms),

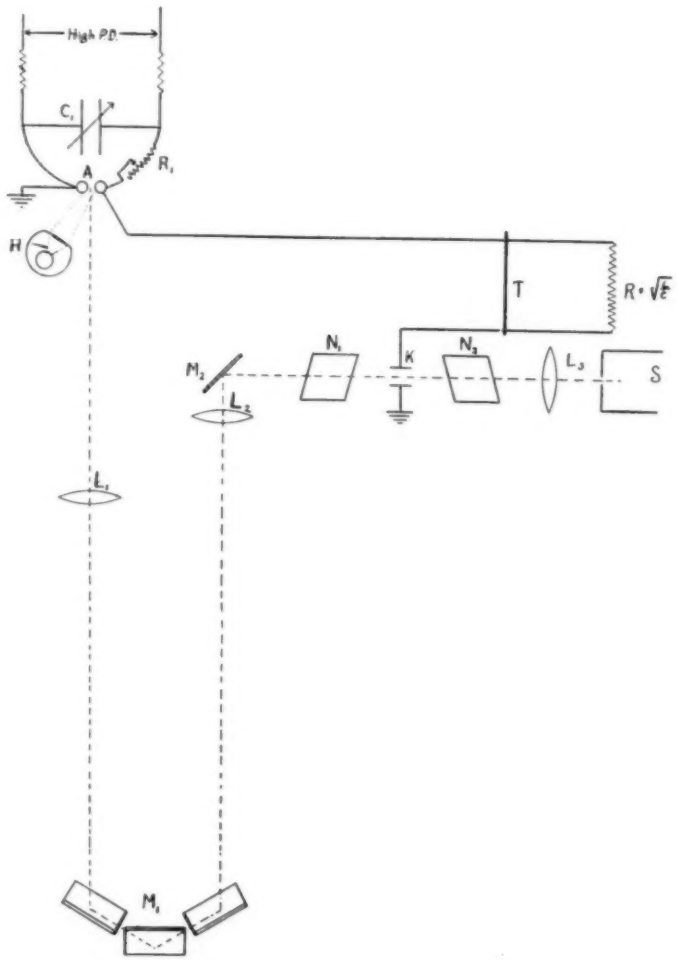


Fig. 2

where L and C are the inductances and capacities per unit length of the wire, is attached across the open ends to prevent possible reflections of the initial transients; while a variable capacity C_1(0.0005 to 0.005 microfarads) and variable resistance R_1 were used to change the conditions in the spark. The circuit containing C_1 is in a plane at right angles to the Kerr cell circuit to avoid unnecessary inductive coupling. The spark gap A was illuminated by a source of ultra-violet light H placed vertically over it and in

a direction at right angles to the direction in which the light of the spark is observed. This reduces the time lag and causes the spark to jump at approximately the same potential each time.

When the spark at A takes place, the potential across it does not fall to its low later value instantaneously.[3] Some recent unpublished work done by Dr. L. B. Snoddy in this laboratory indicates that the exact rate of fall of potential is not completely independent of the circuital factors, as, for example, the rate at which energy is fed into the spark, but that under the conditions here used the potential probably falls to half value within the limits of 10^{-9} to 3×10^{-8} sec. Of the remainder of the potential-time curve very little is definitely known. The fall of potential travels along the lead wires at approximately the velocity of light and starts discharging K at a time equal to the length of lead wire divided by the velocity of light after the beginning of the fall of potential across A. Now since it is possible to reduce the capacity of K to a comparatively small value (4 cm) the rate of fall of potential across K follows roughly the rate of fall across A but at a definite time later.*

If the exact rate of fall of potential across K were definitely known, it would then be possible to compute the time of optical cut-off, since a possible lag in the Kerr effect of CS_2 is at least short enough to be here neglected.[11] Such computations show that the intensity of the light passing N_2 has dropped to $1/e$ of its value by the time that the potential across K falls to 0.77 of its original magnitude. The cell is therefore effectively closed before the potential across K drops to half value. If, then, the amplitude of oscillations in the Kerr cell does not exceed 1/2 the initial potential, when once the cell closes, it does not again effectively re-open.

The fact that the amount of light passing N_2 after the first optical cut-off was too small to effect the results obtained could easily be tested experimentally. The lead wire from A to K was lengthened until one or two lines appeared in the field of view. Then as the mirror system M_1 was slowly moved backward increasing the optical path, the intensity of the lines showed no rapid decreases and, when once they disappeared, did not reappear while the light path was lengthened over 30 meters. This shows that there are no effective short oscillations. Oscillations of longer period were also tested for by placing a mirror rotating at 2000 revolutions per second behind the cell and observing the light flashes passing N_2. The rotating mirror could easily resolve less than 10^{-7} sec, yet the spark appeared when reflected from the mirror as a single sharp image.

It was very easy, however, to introduce oscillations large enough to cause trouble by adding inductance and capacity or by sufficiently lengthening the lead wire from A to K. In fact, with a cell of 4 cm capacity and about 16 meters of lead wire the oscillations become very troublesome, although

* Note: By carefully purifying the CS_2 smaller cells than 4 cm can be used without sacrificing intensity of light passing N_2 for as is well known the dielectric strength of CS_2 can be considerably increased by careful purification.

[11] Beams and Lawrence, Jour. Franklin Inst. **206**, 169 (1928).

longer wires than this have been used successfully. When a low resistance (5.2 ohms) thermocouple galvanometer was placed in series with K and the lead wires lengthened, the readings of the galvanometer, which gave an indication of the magnitude of the oscillations present, increased relatively fast for the first 2 or 3 meters, then increased slowly as more wire was added. Similar observations were made with a wave meter having a vacuum tube voltmeter as an indicator, by means of which an estimate of the amplitude of the oscillations could be obtained. The frequency of course decreased with increase of wire path. A method making use of Lichtenberg figures[12] was also used to get the maximum potential that was applied across the cell after the initial field is relaxed. The method as used here is only approximate but it indicated that the potential never attained more than one half its original value over the wire path range used, at least in the investigation of the air lines.

The fact that the oscillations in K did not have an amplitude greater than one-half the initial potential of the spark might at first seem surprising, but when consideration is taken of the resistance in the spark in its initial stages, the high frequency resistance of the wires, corona losses, etc., this relatively large damping is to be expected. The resistance of the spark gap during its initial stages is not known, but it must fall from a very large value to a comparatively small one in less than the time required for the potential to drop to a low value. If then one-fourth the oscillation period of the Kerr cell circuit is of the same general order of magnitude as that of the time required for the resistance and potential to fall in the spark, the oscillation in the Kerr cell will be highly damped during a part of its first quarter of a period. As the lead wires are lengthened the inductance and capacity of the Kerr cell circuit are increased and hence the amplitude of oscillations, which occur after the initial transient has discharged the Kerr cell, is increased. An increase of lead wire also increases the period of the oscillations as was observed. If, therefore, very long leads are used, it is necessary to introduce resistance. The addition of resistance lengthens the time of optical cut-off, but in most of the work, especially when long leads are used, the cut-off can be slowed down considerably without the introduction of serious complications. The oscillating circuit containing C_1 and A can be changed over a fairly wide range without producing undesirable oscillations in K. This results from the fact that when once the potential across A falls to a low value and the air in the gap is ionized, it does not again rise to a value that, when applied across K, will cause an appreciable amount of light to pass N_2. This condition holds, of course, only when the oscillations in C_1, as in all these experiments, are rapid enough to prevent complete deionization in the gap between half oscillations. Also, since the circuit containing C_1 is not coupled to the circuit containing K except through the spark gap A, oscillations of amplitude large enough to give trouble should not be induced in K even for narrow bands of harmonics, as these, under the given conditions, have too little energy to be effective.

[12] P. O. Pedersen, K. Danske Vidensk. Selkab. **1**, 11 (1919); **4**, 7 (1922); **8**, 10 (1929).

The light after leaving N_2 either is focused on the slit of a spectroscope so that the length of the spark is parallel to the slit, or else the image is examined by means of a direct vision prism. The direct vision prism resolves most of the lines without a slit because of the fact that the spark starts as a narrow thread and expands radially. The air lines appear the full length of the gap. Table I gives the time of appearance of the strong air lines (since it was necessary to use a spectrograph of large light-gathering power and

TABLE I.

Wave-length	Classification[13]		Intensity	Interval (sec. $\times 10^8$)
5011	$1^3P_1'-1^3S_1'$	N II	3	
5007	$1^3S_1'-1^3P_2'''$	N II	4	
5005	$1^3D_3'-1^3F_4'$	N II	10	
5001	$1^3D_2'-1^3F_3'$	N II	10	
	$1^3D_1'-1^3F_2'$	N II		
				0.8
4643	$1^3P_2'-2^3P_1$	N II	8	
4631	$1^3P_2'-2^3P_2$	N II	10	
				1.4
5680	$1^3P_2'-1^3D_3'$	N II	10	
5676	$1^3P_0'-1^3D_1'$	N II	6	
5667	$1^3P_1'-1^3D_2'$	N II	8	

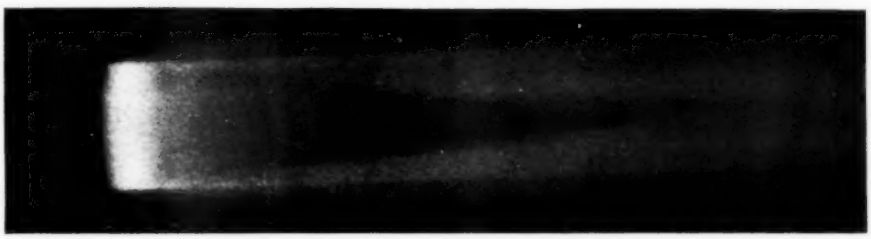
fairly wide slit, the members of the above groups of lines were not clearly resolved.) with respect to the first line that appears. The observations could be repeated with a precision of 3×10^{-9} sec. It will be noted that the order of appearance is not a function of intensity or of wave-length and therefore not the result of the electro-optical dispersion in K. This dispersion in double refraction should make the lines seem to appear in the order of increasing wave-length, but as previously pointed out, is too small to produce serious error under the experimental conditions. When the lead wires were lengthened, the spark lines of the metal appeared as points on the electrodes, followed in turn by the metallic arc lines. The fact that the metallic lines appear in the field of view as points introduces the greatest difficulty in determining the time of their appearance; in fact, some of the previous values for the metallic lines are perhaps somewhat in error due to this cause. Photometric measurements on the rate of increase of intensity of these metallic lines have been attempted but without much success. The rate of evaporation of the metal is apparently variable but a more serious difficulty arises because of the uncertainties of the photographic plate when illuminated with light flashes of short duration.[14] The Clayden effect and other effects that are probably related to it make practically all photographic measurements of light intensities with flashes as short as 5×10^{-8} sec. very unreliable. For example, if a photographic plate is slightly fogged by a weak light as is sometimes done to photograph faint sources of light[15]

[13] Fowler and Freeman, Proc. Roy. Soc. **A114,** 662 (1927).

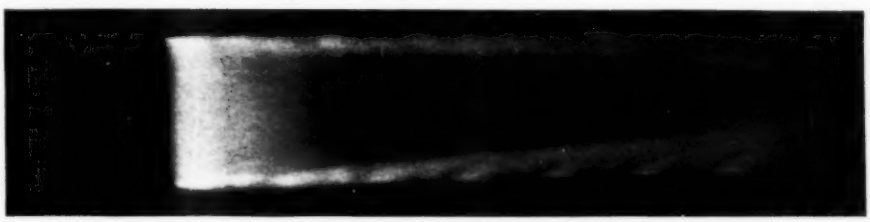
[14] R. W. Wood, Astrophys. J. **17,** 361 (1903). Lüppo-Cramer Grundlagen d. Photographischen Negativverfahren Halle **1,** 608 (1927).

[15] R. W. Wood, Astrophys. J. **27,** 379 (1908).

and then illuminated with a short flash, the image of the flash on the plate is usually reversed. Even when the plate is exposed to the flash alone and care is taken to prevent, as far as possible, fogging by other light, any developer fog is reversed. The intensity of the light is always a factor; a



A. Mg gap. = 7 mm



B. Bi gap = 8mm

C. Bi gap = 8 mm

D. Bi

Fig. 3

faint flash produces a reversal, while a more intense flash gives the ordinary image with usually a reversal around its edges. Attempts have been made to eliminate these troubles but, in the case of flashes less than 5×10^{-8} sec. in duration without much success.

Because of these difficulties with the Kerr cell method when used for observing the metallic lines, as well as the fact that its precision decreases in

the later stages of the spark, a search has been recently made for an independent and complementary method of study. The method finally adopted has been made possible by the development by Henriot and Hunguenard[16] of a means of obtaining high rotational speeds. A mirror 12×12 mm is mounted on a cone shaped piece of metal which rides on a whirling cushion of air. With this arrangement the angular speed is in general limited only by the viscosity of the gas, its molecular velocity and the strength of the rotating parts.

The light from the spark passes through a lens, is reflected by a rotating mirror and falls upon a photographic plate placed at the focus of the lens. Fig. 3, A. B. C. give traces of the image of a spark between magnesium electrodes and bismuth electrodes, each moving 1,300,000 cm/sec. perpendicular to its length. In each case the constants of the circuit are the same. It will be specially noted that the spark first appears as a bright streak completely across the gap. This bright streak fades out very quickly, but the luminosity persists near the electrodes and gradually moves toward the center of the gap. The visible spectrum of the bright streak is composed of air lines and that of the luminous streamers emanating from the electrodes, metallic lines. In the bismuth spark the curved metallic streamers which start from the cathode each half oscillation and move with diminishing velocity until they reach the moving vapor front are very distinct on the original plate. These streamers have been previously observed by several experimenters,[5] but whether they are jets of luminous vapor or pulses of luminosity in the vapor has not yet been completely settled.

Fig. 3 D shows the image of the spark moving parallel to its length. A narrow portion is isolated by a slit perpendicular to the spark to prevent overlapping errors. It will be noted that the spark starts as a thread and expands radially. When the slit was removed or moved to allow only the light from near and including that on the surface of the electrode to reach the plate, and the light dispersed by a prism just before reaching the rotating mirror, the time of appearance of the various spectrum lines could be observed. Similar observations were made when the moving image of the spark fell upon the slit of a spectrograph. The photographs show plainly that the air lines appear first, followed by the spark and later by the arc lines. The technique, however, is not yet developed to a stage where the members of the metallic arc triplets can be distinctly separated, due probably to the photographic errors previously discussed. The limiting factor here seems to be intensity and not angular speed because it is not especially difficult to obtain rotational speeds of 4000 r. p. s. and this can be multiplied several times by simply allowing the light to be reflected from stationary mirrors back to the rotating mirror again. The work, however, is being continued with a better arrangement than that previously used.

The above experiments together with those performed by other investigators[5,17] show definitely that the various spectrum lines in the spark appear

[16] Henriot and Hunguenard, Jour. d. Phys. et Ra. **8**, 443 (1927).
[17] Locher, J.O.S.A. **17**, 91 (1928).

at different times after the beginning of the discharge where by the appearance of a line is meant the time required for the line to become visible through the observing apparatus. However, there is a disagreement in the values obtained by Locher and the writer using similar methods. The difference perhaps lies partly in the larger Kerr cell used by Locher, which would lengthen the time for his cell to cut off. This probably explains, in part at least, why he could not completely extinguish the air lines with lead wires of the same length as his light path, for the intensity of the light passing his cell at maximum voltage was considerably less than that used by the writer so that any errors due to light intensity are in the wrong direction to explain the difference. He also had no way of slowly varying his light path which has been found essential in the above work in testing for troublesome oscillations, or of measuring his time directly in terms of the velocity of light.

The principal factors that determine the appearance of a spectrum line during the initial stages of a spark discharge through a gas must be the average time required to put the atom in the properly excited state by the discharge, the average time it remains excited, and the rate with which it radiates energy when once it starts radiating. In the case of the air lines the sum of the last two factors would be expected from the general results of canal ray experiments[18] to be of the right order of magnitude to explain the observed time between the appearance of the groups of nitrogen lines. This then suggests that in the first stages of the discharge through air where a large number of atoms must be ionized before the potential can fall to a value which will effectively close the cell, that there is a correspondingly large number of atoms multiply ionized and excited to the upper energy levels of the strong air lines. Also, the distribution of excited atoms among the various upper levels of the strong lines probably does not change during the initial stages of the spark. It is possible to study the effect that the average time an atom holds its energy has upon the appearance of spectrum lines in the case of the arc triplets of zinc and cadmium. These triplets have the same upper energy level and therefore should be independent of the conditions of excitation in the discharge. In previous work[7] these lines were found to appear at different times but it has not yet been possible to increase the time-resolving power of the rotating mirror method to a point where a difference in the time of appearance of the lines can be observed. This is necessary before definite conclusions should be drawn because it will then be possible to change the excitation conditions over a very much wider range than was possible with the Kerr cell method and thus make certain any possible effect of the discharge.

The writer is indebted to Professors L. G. Hoxton and C. M. Sparrow of this Laboratory and to Professor E. O. Lawrence of the University of California for many valuable criticisms of part of the work. He is also very grateful to Mr. A. J. Weed, instrument maker, for help in the construction of apparatus.

[18] Wien, Ann. d Physik **66,** 229 (1921); **73,** 483 (1924). McPetrie, Phil. Mag. Series 7, **1,** 1082 (1926).

VIBRATIONAL QUANTUM ANALYSIS AND ISOTOPE EFFECT FOR THE LEAD OXIDE BAND SPECTRA*

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Abstract

Each strong line ($Pb^{206}O$) in the band spectrum emitted by a uranium lead arc in air is represented by three lines ($Pb^{208, 207, 206}O$ with relative intensities in agreement with Aston) in the band spectrum from an ordinary lead arc. The first and second orders of a 21 ft. Rowland grating were used to make this comparison. The observed separations between corresponding band lines of isotopic molecules are in good agreement with the theory of the isotope effect in band spectra with PbO as the emitter.

New measurements of the wave-lengths of the band heads were made from moderate dispersion spectrograms of the ordinary lead arc in air. The bands in the near ultra-violet form a new system**

$$\nu = 30{,}197.0 + [530.6\,(v' + \tfrac{1}{2}) - 1.05\,(v' + \tfrac{1}{2})^2] - [722.3(v'' + \tfrac{1}{2}) - 3.73(v'' + \tfrac{1}{2})^2].$$

Three other systems in the visible have been discussed already by Mecke. Evidence in favor of combining two of these systems (C and B) into one is presented. All of the band systems have a common lower state.

Introduction

THE lead arc in air gives a fairly bright band spectrum consisting of a large number of heads all degrading towards longer wave-lengths. The same spectrum appears with compounds of lead subjected to a variety of conditions of excitation, and consequently there has been a great deal of speculation concerning the identity of the emitter.[1] Using low and moderate dispersion, Eder and Valenta[2] photographed the bands excited upon the introduction of lead chloride into an oxygen illuminating gas flame. They gave wave-length measurements of the heads to four figures, and believed that lead oxide was the emitter. Using the same method of excitation, Lamprecht[3] photographed the visible region at moderate dispersion, and in addition the yellow green region at high dispersion, failing however to resolve the fine structure completely.

Grebe and Konen[4] photographed the spectrum of a carbon arc containing ordinary lead chloride at high dispersion, and repeated using uranium lead

* Paper presented at the Annual Meeting of the A. P. S., New York City, Dec. 28, 1928 (cf. Phys. Rev. **33,** 285 (1929)).

† This work was done at Ryerson Physical Laboratory of the University of Chicago.

** The symbol v is used in this work for the vibrational quantum number.

[1] H. Kayser, Handbuch der Spektroscopie, VI 256.

[2] J. M. Eder und E. Valenta, Atlas Typischer Spektren **17,** Wien, new printing 1924.

[3] H. Lamprecht, Zeits. f. Wiss. Phot. **33,** 10, 16 (1911).

[4] L. Grebe und H. Konen, Phys. Zeits. **22,** 546 (1921).

chloride. They limited themselves to a narrow region in the blue and found that the isotope effect was evident only as a slight wave-length shift and difference in the degree of sharpness of the band spectrum lines compared.

The first part of the present work deals with the vibrational quantum analysis of the lead oxide bands. New measurements of the wave-lengths of the band heads, believed to be more accurate than existing data, are used for most of this analysis. The isotope effect served to guide this part of the work.

In the second part the observed isotope effects will be discussed in detail, and it will be shown that the comparison of the single lines from uranium lead ($Pb^{206}O$) with the corresponding lines in the triplets $Pb^{208, 207, 206}O$ from ordinary lead is in quantitative agreement with the fact that ordinary lead contains isotopes 208, 207, 206.[5] This comparison furnishes a direct test of the theory of the isotope effect in band spectra.

While this work was in progress, and after preliminary reports on the isotope effect had been issued,[6] a short paper by Mecke[7] appeared dealing with his independent work based on Lamprecht's data, leading to a vibrational quantum analysis. These data are not quite complete since Lamprecht gives no measurements of the bands in the red and near ultra-violet. Further details of Mecke's work will be taken up later.

Experimental Procedure

Measurements were made from moderate dispersion spectrograms of the ordinary lead arc in air. In addition comparisons and measurements were made from high dispersion spectrograms in the study of the band structure and isotope effect, and these spectra were taken first with an ordinary lead arc and then with a uranium lead arc. The uranium lead used originated in Belgian Congo ores, and had an atomic weight of 206.1.

The arc electrodes were copper rods $\frac{1}{2}''$ in diameter. A bead of a molten alloy of copper and lead was formed on both the upper $(-)$ and lower $(+)$ electrodes while the arc was in progress by melting pure thin copper wire and lead filings. With the proper proportions of lead and copper in each of the two beads, the arc had a blue color and emitted the lead oxide bands in a satisfactory manner. Fresh lead filings were added at intervals of several hours to prevent the appearance of the green tinge denoting strong emission of the copper spectrum. Copper lines were present on the spectrograms but did not interfere seriously with the work. The red copper oxide bands, generally recorded in a few minutes when the copper arc itself is used, were weak or entirely absent. The current carried was three amperes supplied at 220 volts with a suitable series resistance.

Spectrograms were taken with the Hilger Littrow-mounted El prism spectrograph, having a dispersion with the glass optical system of approximately 21A/mm at 6500A to 6A/mm at 4400A, and with the quartz system of 14A/mm at 4200A to 5.8A/mm at 3200A. The resolution of the structure

[5] F. W. Aston, Nature **120,** 224 (1927).

[6] S. Bloomenthal, Phys. Rev. **33,** 285 (1929). Science **69,** 229, 676 (1929).

[7] R. Mecke, Die Naturwissenschaften **17,** 122 (1929).

lines is incomplete and the heads are single and fairly sharp except where overlapping is great. Exposure of one hour sufficed with the El.

The high dispersion work was done in the first and second orders of the six inch 21 ft. Rowland concave grating having about 14,500 lines per inch and set up in a Rowland mounting. The dispersion in the first order is about 2.63A/mm. The exposure time was usually in excess of 15 hours. Fine grained plates were used in most of the photographic work. Iron lines were placed on the plates before and after exposure. Shifts due to temperature changes were minimized by an efficient system of temperature control consisting of thermostat, fan and heating unit with a mercury current break actuated by a sensitive relay circuit.

Reductions of the measurements of the moderate dispersion plates were made using the Hartmann[8] formula and an automatic Monroe calculating machine. The residuals were small, generally of the order of 0.02A. The formula was applied to only about 200A of the plates at any one time. Kayser's "Schwingungszahlen" served to convert the corrected measurements to vacuum wave-numbers. The iron line wave-lengths selected by the International Astronomical Union served as standards[9] in most of the reductions.

Vibrational Quantum Analysis

In making the assignment of v values the new data on band head wave-lengths, which are believed to be better than the older data, were used. These were supplemented, however, where necessary by older values. This assignment is in agreement with the observed isotope effects (to be described later) using half integral values for the vibrational quantum number following Mulliken,[10] who first found them necessary in the analysis of the BO band spectra. The suggestions of Birge[11] proved useful in evaluating the constants in the empirical frequency equations by means of a consideration of the first and second differences of the wave-numbers in the usual two dimensional matrix diagram.

Assuming that the head is close to the band origin, where the change in rotational energy is approximately zero, one employs the following formula for the frequency of a band head

$$\nu = \nu^0 + \omega_e'(v'+\tfrac{1}{2}) - x'\omega_e'(v'+\tfrac{1}{2})^2 + \omega_e''(v''+\tfrac{1}{2}) - x''\omega_e''(v''+\tfrac{1}{2})^2$$

where ω_e is the frequency of vibration for infinitesimal amplitude and v is the vibration quantum number which takes integral values 0, 1, 2..... Primes (′) and double primes (″) refer, respectively, to the quantity indicated in the upper and lower electronic states.

Mecke assigned the bands in the wave-length region covered by Lamprecht's data to three systems A, B and C. The bands of the C system were extremely weak on the plates taken by the writer, and hence no measure-

[8] A. Hartmann, Astrophys. J. **8,** 218 (1898).
[9] H. Kayser, Op. Cit. VII 405.
[10] R. S. Mulliken, Phys. Rev. **25,** 259 (1925).
[11] R. T. Birge. Nat. Res. Council Bulletin 57, **11,** 123 (1926).

ments were made on such heads. The writer has found an additional system *D* in the region 3209—3594A which was not photographed by Lamprecht. The band head data and vibrational quantum assignments for the *A*, *B* and *D* systems are given in Tables I, II and III.

The data apply to band heads. In the case of PbO the origin of each band as shown by the results of the following paper lies close to the head. *I* is the relative photographic intensity of the band as a whole, λ the wave-length in air in international Angstroms and ν the vacuum wave-number. *O-C* is the difference between the observed wave-number and the value calculated from the proper empirical formulas given below. Under remarks brackets [ ] denote masking by a band of higher frequency whose v values are enclosed. In some cases of masking it was not possible to secure the measurement of a head and the value of the wave-number calculated from the appropriate empirical formula is given in brackets. In such instances the relative intensity estimate was made from the plate enlargement, although the head was not measured. In cases where a measured wave-number value is classified in two systems, evidence justifying this has been found in extensive overlapping of the fine structure examined at high dispersion. The wave-number data for systems *A*, *B* and *D* are from new measurements.

When the suitable v' and v'' values are inserted, the following formulas give the wave-number of a classified band head to within a small difference from the measured value.

For heads in system *A*

$$\nu = 19{,}863.3 + [451.7(v'+\tfrac{1}{2}) - 3.33(v'+\tfrac{1}{2})^2] - [722.3(v''-\tfrac{1}{2}) - 3.73(v''+\tfrac{1}{2})^2]$$

For heads in system *B*

$$\nu = 22{,}289.8 + [496.3(v'+\tfrac{1}{2}) - 2.33(v'+\tfrac{1}{2})^2] - [722.3(v''+\tfrac{1}{2}) - 3.73(v''+\tfrac{1}{2})^2]$$

For heads in system *D*

$$\nu = 30{,}197.0 + [530.6(v'+\tfrac{1}{2}) - 1.05(v'+\tfrac{1}{2})^2] - [722.3(v''+\tfrac{1}{2}) - 3.73(v''+\tfrac{1}{2})^2]$$

Because of the fact that the isotope effect is unresolved at moderate dispersion, the constants given in these formulas are but approximations.

It is evident from inspection of these equations that all three systems have a common final state, which is probably the normal state of the PbO molecule. The systems *A*, *B* and D arise then from transitions from 2.5, 2.8, and 3.7 volt electronic levels, respectively, to this common lower state.

Mecke's equations based on Lamprecht's data are

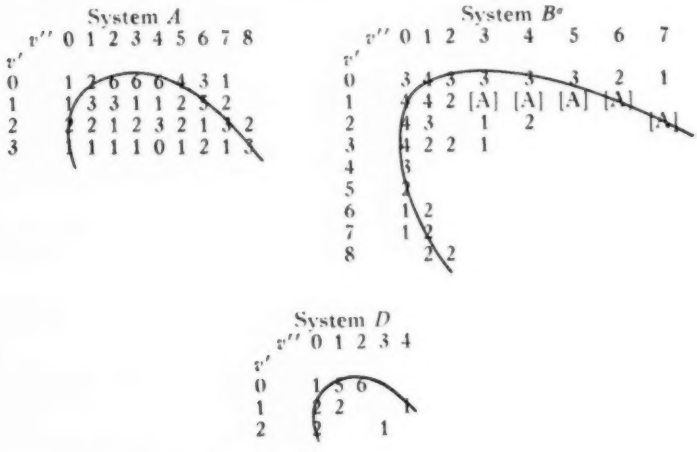
(*A*) $\nu = 19{,}877 + [445(v'+\tfrac{1}{2}) - 1(v'+\tfrac{1}{2})^2] - [722(v''+\tfrac{1}{2}) - 3.5(v''+\tfrac{1}{2})^2]$

(*B*) $\nu = 22{,}293 + [498(v'+\tfrac{1}{2}) - 1.4(v'+\tfrac{1}{2})^2] - [722(v''+\tfrac{1}{2}) - 3.5(v''+\tfrac{1}{2})^2]$

(*C*) $\nu = 24{,}875 + [537(v'+\tfrac{1}{2}) - 15(v'+\tfrac{1}{2})^2] - [722(v''+\tfrac{1}{2}) - 3.5(v''+\tfrac{1}{2})^2]$

System *D* is missing from Mecke's analysis since Lamprecht failed to secure wave-number data below 3740A. Although the new equations of *A* and *B* are similar numerically to Mecke's, the writer believes that his equations

TABLE I. *The A bands. New data and vibrational quantum analysis.*



[a] The intensity data of Table I for system *B* comes from Lamprecht's data. [A] denotes masking by *A* heads. These superposed bands are unusually strong in some cases.

v'	v''	I	λHd. (I.A)	ν(cm^{-1})	O-C (cm^{-1})	Remarks
0	7	1	6720.32	14,876.2	−4.3	
2	8	2	6620.23	15,101.1	− .1	
1	7	2	6524.25	15,323.2	−2.3	
3	8	3	6433.63	15,539.0	6.2	
6	6	3	6427.73	15,553.3	2.6	
2	7	333	6342.01	15,763.5	− .4	
1	6	5	6250.75	15,993.4	−2.3	
3	7	1		[16,195.6]		[0,5]
0	5	4	6160.52	16,227.9	− .4	
2	6	1d		[16,434.1]		
1	5	2		[16,673.3*]		[Pb 6002.0]
3	6	2		[16,865.8]		[0,4]
0	4	6	5910.74	16,913.7	.3	
2	5	2	5842.13	17,112.3	.6	
1	4	1d		[17,358.4]		[0,3]
3	5	1		[17,543.5]		[0,3]
0	3	6	5677.78	17,607.6	1.7	
2	4	3	5617.65	17,796.1	− .7	
1	3	1		[18,050.9]		[0,2]
3	4	0		[18,228.5]		[0,2]
0	2	6d	5459.38	18,312.0	6.2	also 2,7 B
2	3	2	5407.18	18,468.8	− .5	also 1,6 B
1	2	3	5331.11	18,752.6	1.7	
3	3	1		[18,921.1]		[0,1]
0	1	2	5258.26	19,012.4	− .9	
2	2	1	5211.98	19,181.2	8.1	
1	1	3	5138.18	19,457.4	−1.0	
3	2	1	5093.19	19,628.6	7.6	
0	0	1	5068.78	19,723.1	−5.0	
2	1	2	5024.21	19,898.1	−1.4	
1	0	1		[20,233.1]		[0,2 B]
3	1	1	4916.62	20,333.5	−5.1	
2	0	2	4850.12	20,612.1	− .6	
3	0	1	4747.81	21,047.7	−3.4	

* Eder and Valenta give λ5998A (ν = 16,667.6).

fit the new data better than Mecke's do the data of Lamprecht. Mecke assigned the three systems A, B and C to a $^3\pi \rightarrow {}^3\Sigma$ transition, but the fine structure analysis to be reported in a companion paper does not justify this

TABLE II. *The B bands. New data and vibrational quantum analysis.*

v'	v''	I	λ Hd. (I.A)	ν(cm^{-1})	O-C (cm^{-1})	Remarks
0	7	1	5770.01	17,326.2	−3.3	
0	6	1	5553.83	18,000.6	− .9	
2	7	2	5459.38	18,312.0	4.1	also 0,2 A
1	6	2	5407.18	18,488.8	1.6	also 2,3 A
0	5	3	5353.82	18,673.1	−4.7	
1	5	0		[19,168.1]		[2,2 A]
0	4	6	5162.31	19,365.8	3.3	
1	4	0		[19,853.2]		[0,3]
0	3	6	4983.79	20,051.4	3.6	
2	4	1	4916.80	20,341.0	− .3	
1	3	0		[20,545.7]		[2,0 A]
0	2	6	4816.90	20,754.5	.5	
2	3	1	4753.55	21,031.1	2.3	
1	2	2	4706.43	21,241.6	4.1	
0	1	5	4657.98	21,462.5	− .2	
3	3	1	4647.49	21,511.1	4.2	
2	2	1		[21,733.4*]		[1,1]
1	1	6	4553.71	21,954.0	−1.0	
0	0	1	4509.23	22,170.5	6.7	
3	2	1	4499.99	22,216.1	− .7	
2	1	1	4454.80	22,441.4	− .7	
1	0	5	4410.38	22,667.4	.5	
3	1	0		[22,922.7†]		[2,0]
2	0	4	4317.06	23,157.4	−1.8	
3	0	4	4229.01	23,639.6	−2.0	
4	0	2	4145.93	24,113.3	1.5	

* Lamprecht gives λ4597.9 (ν=21,743) (doubtful)
† Lamprecht gives λ4358.3 (ν=22,938)

designation. Furthermore it has been noticed that practically all the bands belonging to system C can be accounted for equally well as members of B.

It has been remarked previously that the bands of system C in the region from 4280A to 3740A were not sufficiently strong to be measured on the

TABLE III. *The D bands. New data and vibrational quantum analysis.*

v'	v''	I	λ Hd. (I.A)	ν(cm^{-1})	O-C (cm^{-1})	Remarks
1	4	1	3594.16	27,815.0	− .3	
0	2	6	3485.68	28,680.6	1.1	
2	3	1	3442.76	29,038.2	4.6	
0	1	5	3401.92	29,386.9	0	
1	1	2	3341.83	29,915.2	.1	
0	0	1	3320.68	30,105.7	3.7	
1	0	2	3264.36	30,625.1	−4.9	
2	0	2	3209.21	31,151.3	−4.5	

plates taken by the writer. On the other hand, Lamprecht's data do not extend beyond 3740A where the heads of the D system occur. Thus the older data in this region cannot be corrected to conform to the measurements made by the writer. Employing, therefore, Lamprecht's data for all the heads of

the bands in this region an equation for the B system is found including practically all of the heads of system C.[12] The equation is

$$\nu = 22,292 + [495.7(v'+\tfrac{1}{2}) - 2.05(v'+\tfrac{1}{2})^2] - [722.3(v''+\tfrac{1}{2}) - 3.73(v''+\tfrac{1}{2})^2]$$

The observed minus calculated values obtained from this equation are well within the experimental error of the measurements given by Lamprecht. It is obvious that this equation differs but little from the equation for the B system

TABLE IV. *Unidentified heads in the lead oxide band Spectrum.*[b]

λ Hd. (I.A)	$\nu(cm^{-1})$	I	Investigators	Remarks
6680	14,966	2[g]	Eder and Valenta	also 6677.77 (1) S.B
6476	15,437	2	Eder and Valenta	also 6475.78 (1) S.B
6288	15,899	1	Eder and Valenta	b
6210	16,099	2	Eder and Velanta	b
6021	16,604	1	Eder and Valenta	b
5858	17,066	1	Eder and Valenta	d
4784.9	20,893	2	Lamprecht	b
4694	21,289	1	Eder and Valenta	c 4692.94 (1) S.B.
4632	21,583	2	Eder and Valenta	d
4619	21,644	1	Eder and Valenta	d
4369.4	22,880	1	Lamprecht	e
4281.2	23,351	1	Lamprecht	b
4156.3	24,053	2	Lamprecht	b
4036.2	24,769	2	Lamprecht	b
3950.6	25,306	1	Lamprecht	e
3878.3	25,777	1	Lamprecht	e
3839.6	26,037	1	Lamprecht	e
3804.9	26,275	1	Lamprecht	f 3810.61 (1) S. B.
3771.8	26,505	1	Lamprecht	e
3748	26,673	1	Eder and Valenta	d
3736.3	26,757		Lamprecht	e
3557	28,106	1	Eder and Valenta	f 3554.43 (1) S.B.

[a] Observed also by Lamprecht but not by S. B.
[b] Observed also by Eder and Valenta but not by S. B.
[c] Observed also by S. B. but not by Lamprecht.
[d] Observed by neither Lamprecht nor S. B.
[e] Observed by neither Eder and Valenta nor S. B.
[f] Observed also by both Eder and Valenta and by S. B.
[g] The relative intensity estimates for Eder and Valenta's data were made by the writer from an examination of the PbO spectra in the Atlas.
[h] These unidentified heads cannot be accounted for even if Mecke's system C is included with the other three systems. Many of these heads represent, no doubt, the superposition of a number of lines.

based upon the new data. However, until new data are obtained one may reasonably assume that thus far only three systems are known to be present in the spectrum of PbO, namely A, B, and D.

Table I illustrates the experimental intenstity data. Comparison with the Franck-Condon theory is postponed until a fine structure analysis yields further data concerning the molecular constants of PbO.

BAND STRUCTURE AND ISOTOPE EFFECT

Under high dispersion each band consists apparently only of a P and R branch, which run coincident near the head of each band. Because of the fine

[12] The heads not included in B are 4281.2A, 4156.3A and 4036.2A.

scale of the band structure and overlapping of series, it is difficult to make accurate measurements of the wave-lengths of the individual lines. The bands in the red, yellow and green, photographed already at high dispersion with the uranium lead arc as source, appear to offer the best possibilities for a fine structure analysis. Such an analysis has been made already for some of the bands, and the results are given in a subsequent paper in collaboration with Dr. A. Christy.

The expression for the separation in wave-numbers between the corresponding band spectrum lines of two isotopic diatomic molecules[13] is

$$\nu_2-\nu_1=(\rho-1)\left[(v'+\tfrac{1}{2})w_{e1}'-(v''+\tfrac{1}{2})w_{e1}''\right]$$
$$-(\rho^2-1)\left[(v'+\tfrac{1}{2})^2x_1'w_{e1}'-(v''+\tfrac{1}{2})^2x_1''w_{e1}''\right]-(\rho^2-1)(\nu_1-\nu_{Hd})$$

where $\rho=(\mu_1/\mu_2)^{1/2}$ and $\mu_1=m_1m/m_1+m$, $\mu_2=m_2m/m_2+m$. m_1 and m_2 are the masses of the isotopic atoms and m is the mass of the common kind of atom in the molecules m_1m and m_2m. Subscript 1 refers to the constant for the more abundant and subscript 2 to that for the less abundant molecule. In our case m_1 is the mass of Pb^{208}, and m_2 the mass of Pb^{207}. For convenience one can make the following abbreviations.

$$\Omega=(\rho-1)\left[(v'+\tfrac{1}{2})w_e'-(v''+\tfrac{1}{2})w_e''\right]$$
$$o=-(\rho^2-1)\left[(v'+\tfrac{1}{2})^2x'w_e'-(v''+\tfrac{1}{2})^2x''w_e''\right]$$
$$\tau=(\rho^2-1)(\nu-\nu_{Hd}).$$

The subscript 1 is dropped above since the isotope effect is unresolved at moderate dispersion.

$$\nu_2-\nu_1=\Omega+O+\tau.$$

Neglecting the rotational contribution τ and also the term O, the approximate magnitude of the (vibrational) isotope effect can be calculated simply by the relation

$$\nu_2-\nu_1=(\rho-1)(\nu-\nu^0)$$

where ν^0 is the wave-number of the band system origin. ρ for PbO is $[(208\times16)(207+16)/(208+16)\ (207\times16)]^{1/2}=1.000173$. This is approximately equal to $[(207\times16)(206+16)/(207+16)\ (206\times16)]^{1/2}$. Hence in the A system where $\nu^0=19{,}863.3$ and ν for the head of the 0,5 band is 16,227.9, then $\nu_2-\nu_1=-0.63$ cm^{-1}. This is close to the observed value -0.68 ± 0.05 determined by direct comparison of the lines $Pb^{206}O$ from uranium lead with the lines $Pb^{208,\,207,\,206}$ O from ordinary lead. If Pb_2 were the emitter, then

$$\rho=[(208\times207)(207+207)/(208+207)(207\times207)]^{1/2}=1.0015,$$

and the isotope separation $\nu_2-\nu_1$ for the 0,5A band ought to be about 5.5 wave-numbers, almost nine times as large as the value actually observed.

[13] R. S. Mulliken, Phys. Rev. **25**, 119 (1925) and F. W. Loomis, Nat. Res. Council Bulletin 57, **11**, 123 (1926). The last term in this formula is only an approximation.

Figure 1 illustrates the isotope effect observed near the head of the λ5677.78A (0,3*A*) band. The upper microphotometer record was secured from a spectrogram taken with uranium lead of atomic weight 206.1 in the arc. Below is the record of the same region on a spectrogram taken with ordinary lead (atomic weight 207.2) in the arc. A Moll microphotometer, which records automatically was used. The central reference line is a lead arc line of wave-length 5692.329A which probably shows a small atomic isotopic effect. The light vertical lines serve to identify the corresponding

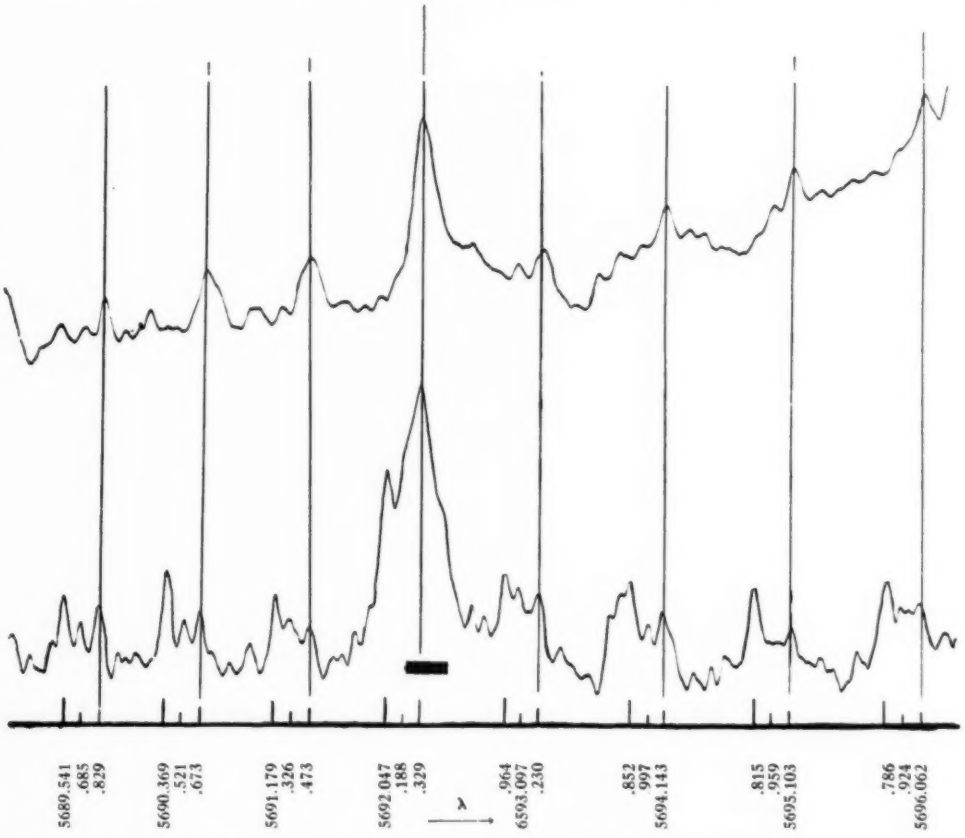


Fig. 1. Isotope effect in the λ5677.78 (0,3 *A*) band of PbO. Above, $Pb^{206}O$ from uranium lead. Below, $Pb^{208,\ 207,\ 206}O$ from ordinary lead. Isotopic displacement −0.428 wave-numbers.

lines in the two spectra, namely $Pb^{206}O$. The lines $Pb^{208}O$ and $Pb^{207}O$ are apparently absent from the upper trace. Isotope 208 is the most abundant in ordinary lead, and hence $Pb^{208}O$ gives the strongest lines. Aston gives 208 (7), 207 (3), and 206 (4) as the composition of ordinary lead, and the results of this investigation are in agreement with these relative abundancies. The wave-lengths of the series lines are given in the lower part of the figure.

Figure 2 gives a similar comparison near the head of the λ6160.52A (0,5*A*) band. Just as in the case of the 0,3 band, the lines $Pb^{206}O$ are on the long wave-length side of the lines $Pb^{207}O$. The *P* and *R* lines are coincident

in the middle of the picture and begin to diverge both on the far left and far right side, causing the lines to become fuzzy. The single lines $Pb^{206}O$ in the upper spectrum were secured with a heavy exposure in order to bring out weak lines of other isotopic molecules that might possibly be present. This was done in an attempt to satisfy Dr. C. S. Piggot's[14] wish for a reliable qualitative analysis of uranium lead from the Belgian Congo. Data of this

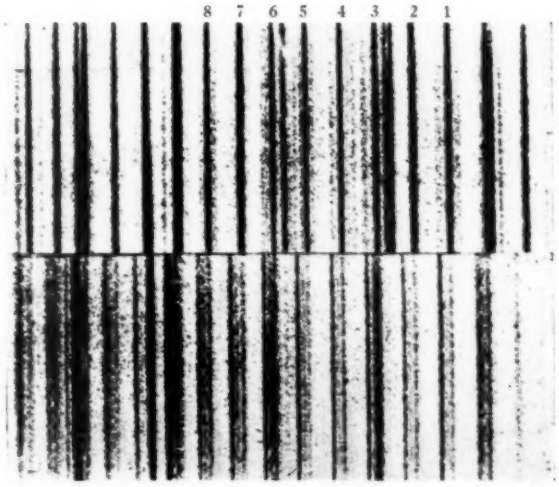


Fig. 2. Isotope effect in the λ6160.52A (0,5 *A*) band of PbO.

nature are necessary in estimating the age of uranium minerals. It is evident from inspection of Fig. 2 that 206 is the principal isotope in the uranium lead sample used. This is to be expected from its atomic weight of 206.1.

Table V gives the measured wave-lengths of the band lines examined in Fig. 2. The first order of the grating was used. The numbers above the lines $Pb^{206}O$ in Fig. 2 correspond to those under "group" in Table V.

TABLE V. *Wave-lengths of lines in the 6160.52 A (0,5A) band.*

Group	$Pb^{206}O$	$Pb^{207}O$	$Pb^{208}O$
1	6204.916	6204.685	6204.434
2	3.327	3.077	2.800
3	1.717	1.461	1.174
4	0.117	6199.890	6199.653
5	6198.583	8.369	8.108
6	7.086	6.827	6.577
7	5.662	5.386	5.125
8	4.213	3.973	3.707

Figure 3 illustrates the isotope effect observed in one of the *D* system bands. The band lines in the upper half of the figure are the lines $Pb^{206}O$ from uranium lead. These are shifted 0.036 ± 0.01A on an average approximately to longer wave-lengths with respect to the lower lines $Pb^{208, 207, 206}O$ from

[14] C. S. Piggot, Jour. Wash. Acad. of Sciences **18**, 10, 269 (1928).

ordinary lead, which are unresolved in this region. Table VI gives the wave-length data. These begin, reading from right to left, with the second line on the short wave-length side of the reference line in Fig. 4. It is to be noted that here the isotope effect is unresolved although the second order of the grating was used. This is in marked contrast to the effects observed in system *A*, but is in agreement with the shift calculated on the basis of the vi-

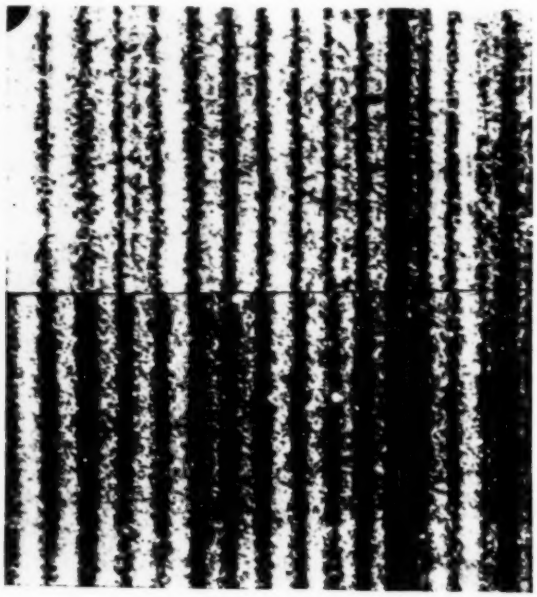


Fig. 3. Isotope effect in the λ3485.68A (0,2 *D*) band of PbO. Upper spectrogram, uranium lead oxide. Lower spectrogram, ordinary lead oxide.

brational assignment for the *D* bands. The calculated shift is -0.271 cm^{-1} for $Pb^{208}O$ as compared with $Pb^{207}O$ while the value measured is -0.30 ± 0.08 cm^{-1}. The minus sign indicates that the lines from the molecules containing the lighter isotope are displaced towards lower frequencies with respect to the radiations from the molecules containing the heavier isotope.

TABLE VI. *Wave-lengths of lines in the λ3485.68A (0,2D) band.*

$Pb^{206}O$ (From uranium lead)	$Pb^{208,\ 207,\ 206}O$ (unresolved) (From ordinary lead)
3490.106	3490.078
.372	.343
Fe 3490.577	Fe 3490.577
.632	.579
.922	.895
1.236	1.168
.501	.458
.807	.773
2.108	2.081
.443	.390

Table VII gives a comparison between the observed isotope effects and the values calculated as the sum $\Omega+O+\tau$.

In the 0,3 band of system *A* the lines which we now recognize as $Pb^{208}O$ and $Pb^{206}O$ were measured by Lamprecht in 1911, who designated them as lines of series I and III in his tables of wave-lengths. The lines $Pb^{207}O$, which form the intermediate series, are missing from the data of Lamprecht, since he used lower dispersion and resolving power than did the writer.

TABLE VII. *Isotope effects observed by direct comparison of $Pb^{208}O$ from uranium lead with $Pb^{208\cdot207\cdot206}O$ from ordinary lead, and the values calculated as the sum $\Omega+o+\tau$.**

in Band	$\nu-\nu$Hd. (cm^{-1} approx.)	$\lambda_2-\lambda_1$(I.A.) Observed	$\nu_2-\nu_1$(cm^{-1})	Ω	O Calculated (cm^{-1})	τ	$\nu_2-\nu_1$ (cm^{-1}) Calculated	Observers	Remarks
0,5*A*	− 78	0.255± .02	−0.68± .05	−0.648	+0.039	−0.027	−0.636	S. B.	Resolution into Triplets
0,3*A*	− 47	0.141± .02	−0.43± .06	−0.398	+0.016	−0.016	−0.398	S. B.	Resolution into Triplets
3,0*B*	−116	−0.055± .02	+0.31± .11	+0.238	−0.010	−0.040	+0.188	Grebe and Konen	Not Resolved
0,2*D*	− 36	0.036± .01	−0.30± .08	−0.267	+0.008	−0.012	−0.271	S. B.	Not Resolved

* The isotope effect calculated here is that of $Pb^{208}O$ and $Pb^{207}O$ and is approximately the same as that of $Pb^{208}O$ and $Pb^{206}O$ numerically.

Dr. R. S. Mulliken suggested this problem and gave a good deal of important advice in the course of this investigation. Consequently the writer takes this opportunity to thank him. To Drs. Gale, Compton, Harkins, Piggot, Hoag and Christy, the writer feels indebted for many helpful hints. The uranium lead of atomic weight 206.1 was a gift from the Wolcott Gibbs Memorial Laboratory of Harvard University, and the writer is indebted through Dr. Mulliken to Dr. L. P. Hall for making about 20 grams of pure material extracted from Belgian Congo uranium ores available.

When Dr. Mecke was informed of the present investigation, he very kindly agreed to leave further work on the fine structure analysis to the writer.

FINE STRUCTURE ANALYSIS OF THE BANDS IN THE A AND D SYSTEMS OF LEAD OXIDE

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(Received November 19, 1929)

Abstract

The bands of the A and D systems of PbO are composed of single R and P branches only. The combination principle has been applied to the lines of these branches and the rotational constants of the molecule have been determined. The bands of PbO have been assigned previously to three systems, A, B, and D, all three having the final state in common. The nuclear separation of this final state is found to be 1.9207×10^{-8} cm, that of the upper state of A, 2.0927×10^{-8} cm, and of the upper state of D, 2.0424×10^{-8} cm. No Q branches have been found in either of the two systems, indicating that all the electron states involved have the same value of Λ. It is shown that the electronic levels of the two systems investigated are singlets. All the electron states involved are, in all probability, $^1\Sigma$ states.

THE purpose of this work is to determine the rotational constants of the lead oxide molecule and if possible its electron states. The vibrational analysis and the isotope effect are treated in the preceding paper, in which it is also shown that practically all the bands in the spectrum of PbO may be assigned to three systems, A, B, D, all having the final electron states in common.

The following bands were used for the fine structure analysis:

0,2 λ5459.4 A system	0,5 λ6160.5 A system
0,3 λ5677.8 A system	0,2 λ3485.7 D system

The spectrograms[1] from which the lines were measured were taken with a sample of uranium lead of atomic weight 206.1. The stronger lines, therefore, are due to $Pb^{206}O$. In addition to these, however, there are, near the head of each band, especially in those of $A(0,2)$, $A(0,3)$, and $A(0,5)$, fainter lines due to $Pb^{208}O$. It cannot be determined with any certainty whether or not lines due to $Pb^{207}O$ are present. If the lines of $Pb^{208}O$ are due to the fact that the uranium lead has been contaminated with ordinary lead, we should expect the lines of $Pb^{207}O$ to appear with intensity approximately half as great as those of $Pb^{208}O$.[2] Since most rocks contain traces of ordinary lead, it may be that in the process of extraction uranium lead has been contaminated with ordinary lead. Furthermore the atomic weight of pure uranium lead was found to be 206.06[3] while the atomic weight of the sample

[1] For a detailed account of the experimental work, see preceding paper.

[2] Aston, Nature **120**, 224 (1927). Ordinary lead consists of isotopes 208, 207, 206, in the ratio of 7, 3, 4.

[3] G. Kirsch, "Geologie und Radioaktivitat" p. 138.

from which these spectrograms were made was 206.1, indicating that the sample used must have contained traces of ordinary lead.

The lines of the λ5677.8 A and λ6160.5 A bands were measured from first order plates, those of the other two from second order plates. The measurements of individual lines are considered to be accurate to within 0.1 cm^{-1}.

The bands of the two systems which were examined consist of single R and P branches, indicating that we have to do with a transition between two singlet electron levels having the same $\Lambda(^1\Sigma - {}^1\Sigma$ or perhaps $^1\Pi \rightarrow {}^1\Pi)$. In the more favorable cases, for large rotational quantum numbers, lines from the R and P branches fall in such a way as to form close doublets, the doublets becoming single lines as they approach the head. All the bands of PbO so far investigated degrade to the red.

Assuming rotational terms of the form

$$\text{const} + BJ(J+1) - DJ^2(J+1)^2 + \cdots$$

where[4] $B = B_v = B_0 - \alpha v = B_e - \alpha(v+1/2)$, we may define the usual combination differences $\Delta_2F'(J)$ and $\Delta_2F''(J)$ as

$$R(J) - P(J) = \Delta_2F'(J)$$

and

$$R(J-1) - P(J+1) = \Delta_2F''(J)$$

$\Delta_2F(J)$ being

$$\Delta_2F(J) = 2(B-2D) + 4(B-3D)J - 12DJ^2 - 8DJ^3 + \cdots$$

$\Delta_2F'(J)$ should be the same for the (0,2), (0,3), and (0,5) bands of the A system, and $\Delta_2F''(J)$ should be the same for the (0,2) band of the A system and for the (0,2) of D, since both these systems have the final level in common. These combinations have been found and tested for over thirty members, at least, of the R and P branches in each of the above bands. Samples of values for $\Delta_2F^{(0)\prime}$ of the A system for the three bands mentioned above are given in Table I, while the corresponding values of $\Delta_2F^{(2)\prime\prime}$ of (A) and (D) are given in Table II.[4a] The values of $\Delta_2F^{(3)\prime\prime}(A)$, $\Delta_2F^{(5)\prime\prime}(A)$ and $\Delta_2F^{(0)\prime}(D)$, for small, medium, and large values of J, are given in Table III, columns 2, 3, and 4. The correct value of J is given in column 1 of the latter three tables. The occasional large discrepancies between the corresponding Δ_2F values in Tables I and II are due partly to over-lapping of the two branches R and P, especially in the regions near the head, and partly to the superposition of lead and copper lines or their ghosts on the lines of the bands. It is thought inadvisable at present to give more complete tables of Δ_2F values or tables of the wave-numbers of the lines which have been measured in all these bands. These tables will be given later, when a more thorough investigation of these three systems of the PbO molecule has been made.

[4] The symbol v is used in this work for the vibrational quantum number.

[4a] In $\Delta_2F^{(0)\prime}$, $\Delta_2F^{(2)\prime}$, etc., the subscript of F indicates the value of the vibrational number v.

The constants of the molecule were obtained by the graphical method outlined on pp. 172–173 of the Report.[5] The values of Δ_2F/J were plotted

TABLE I. *Samples of values of* $\Delta_2F^{(0)}{}'$ *for* $A(0,2)$, $A(0,3)$, *and* $A(0,5)$.

J	$A(0,2)$	$A(0,3)$	$A(0,5)$
10		10.8	
11		11.2	
12		12.8	
20		21.1	21.2
21		21.8	22.0
22		23.2	23.0
35	36.4	36.6	36.1
36	37.5	37.8	37.2
37	38.9	38.7	39.1
47	48.7	48.9	48.8
48	49.7	50.1	49.8
49	50.7	51.0	50.9
56	57.8	57.9	57.8
57	59.3	58.9	58.9
58	59.9	59.8	59.9
66	67.7	67.9	68.0
67	68.6	68.8	68.9
68	69.7	69.9	69.7
76	77.9	77.8	
77	79.0	79.1	
78	79.7	79.7	

TABLE II. *Samples of values of* $\Delta_2F^{(2)}{}''$ *of* $A(0,2)$ *and* $D(0,2)$.

J	$A(0,2)$	$D(0,2)$
25		29.8
26		31.3
27		33.2
36	44.1	43.9
37	45.3	45.5
38	46.9	46.7
47	57.4	57.3
48	58.4	58.4
49	59.7	59.5
56	68.6	68.1
57	69.4	69.3
58	70.5	70.5
65	78.8	79.0
66	79.8	79.2
67	81.1	81.4
74	89.1	
75	90.8	
76	91.9	
83	100.0	
84	101.1	
85	102.5	

against J, and from this plot the values of B and D were calculated. The value of D found by this method is the same, within experimental error,

TABLE III. *Values of* $(A)\Delta_2F^{(3)}{}''$, $(A)\Delta_2F^{(5)}{}''$, *and* $(D)\Delta_2F^{(0)}{}'$, *for small medium and large J.*

J	$(A)\Delta_2F^{(3)}{}''$	$(A)\Delta_2F^{(5)}{}''$	$(D)\Delta_2F^{(0)}{}'$
11	13.7		
12	14.9		
18	22.1	22.0	
19	23.4	23.2	
23	28.2	27.5	24.8
24	29.7	29.1	25.8
25	30.8	30.4	26.5
41	49.9	49.0	44.9
42	51.1	50.5	45.6
43	52.4	51.4	46.8
66	79.5	78.4	71.6
67	80.8	79.6	72.4
68	81.8	80.9	73.5
75	90.2		
76	91.4		
77	92.4		

[5] National Research Council Bulletin, Report on "Molecular Spectra in Gases," Vol. 11, part 3, 1926.

as that obtained by the formula $D=4B_0^3/\omega_0^2$. The constants of the molecule for the three electronic levels are given in Table IV.

TABLE IV. *Rotational constants of the $Pb^{206}O$ molecule.*

Final states of systems A and D*	
$B_0''=0.3063$ cm^{-1}	$B_2''=0.3025$ cm^{-1}
$B_3''=0.3007$ cm^{-1}	$B_5''=0.2967$ cm^{-1}
$D_0''=2.203\times10^{-7}$ cm^{-1}	$\alpha''=0.0019$
$r''_0=1.9207\times10^{-8}$cm	
Initial state of A	
$B_0'=0.2579$ cm^{-1}	$D_0'=2.7856\times10^{-7}$ cm^{-1}
$\alpha'=0.0022$	
$r_0'=2.0927\times10^{-8}$ cm	
Initial state of D	
$B_0'=0.2707$ cm^{-1}	$D_0'=2.8183\times10^{-7}$ cm^{-1}
$\alpha'=0.0006$	
$r_0'=2.0424\times10^{-7}$ cm	

* These systems have the final state in common.

It is estimated that the values of B are accurate to within 0.1 percent, hence the calculated values of r_0 (nuclear separation) should be accurate to within 0.05 percent. In this analysis the value of B_0'' was not obtained directly but was extrapolated from the known values of B_2'', B_3'', and B_5''. Since B_2'' was obtained from two bands, i.e. 0,2 of (A) and 0,2 of (D), twice as much weight was given to this value as to the two others.

R. T. Birge[6] has found the following empirical equation from a study of a large number of bands: $2B_0x/\alpha=1.4\pm2$. Substituting the corresponding values for the lower electronic level of the A system we find: $2\times3.73\times30616/722.3\times0.0183=1.7$. Using this value for the above fraction, α for the upper electronic levels for the systems A and D was calculated. In calculating r_0, the atomic weight of uranium lead was taken to be 206.06.[4] In all the calculations the values of the auxiliary constants used are those given by Birge.[7]

It has been remarked above that in all the bands investigated no Q branches were observed.[8] The absence of a strong Q branch indicates that $\Delta\Lambda=0$.[9] The only possibilities, therefore, are that we are dealing with such transitions as $^1\Sigma\rightarrow{}^1\Sigma$, $^1\Pi\rightarrow{}^1\Pi$, $^1\Delta\rightarrow{}^1\Delta$, etc. It has been stated that the bands of the A and D systems consist of single R and P branches. Thus it is not possible that either the upper or lower levels of the system or both are narrow multiplets, for, in that case, we would expect additional branches to appear. It is evident, therefore, that the levels in question are singlets. (The bands of the B system have also been examined with this fact in mind. As far as can be ascertained from a cursory investigation of enlargements

[6] R. T. Birge, Phys. Rev. **31**, 919 (1926).

[7] R. T. Birge, Phys. Rev. Supplement **1**, 1 (1929).

[8] R. Mecke, Die Naturwissenschaften **17**, 133, stated that the three systems A, B, and C are probably due to a $^3\Pi\rightarrow{}^3\Sigma$ transition, the upper electron states of A, B, and C being the components of the $^3\Pi$ state. It has been shown in the preceding paper that practically all the bands assigned by Mecke to system C are actually members of system B. This work shows that system A is not due to a $^3\Pi\rightarrow{}^3\Sigma$ or even to a $^1\Pi\rightarrow{}^1\Sigma$ transition.

of these bands, their appearance is similar to those of the other systems. If there is a Q branch in these B bands, it must be very weak.)

R. S. Mulliken[9] has given the theoretical intensities to be expected in transition between two singlet electronic levels, both of which have the same value of Λ. The equations are:

$$i_Q = a(2J+1)\Lambda^2/J(J+1)$$
$$i_P = a(J^2-\Lambda^2)/J$$
$$i_R = [a(J+1)^2-\Lambda^2]/J+1$$

In these equations the Boltzmann factor has been omitted, since for low values of J and B and high temperatures this factor is essentially equal to 1. It may be shown readily from the above equations that if $\Lambda = 1, {}^1\Pi \rightarrow {}^1\Pi$, there is a weak Q branch; the intensity of the first Q line is three times as great as that of the first R line, the itensities of the other Q lines, however, decrease rapidly for higher values of J. For $\Lambda = 2, {}^1\Delta \rightarrow {}^1\Delta$, we have qualitatively the same result but the first Q line is very much stronger, and the intensities of the other lines decrease less rapidly.

It is obvious from an examination of the plates and enlargements of these bands that we do not have a ${}^1\Delta \rightarrow {}^1\Delta$ transition, for in that case a Q head should be strong enough to show and there is no evidence of such head in our plates. The only alternative, therefore, is that the bands are due either to ${}^1\Pi \rightarrow {}^1\Pi$ or ${}^1\Sigma - {}^1\Sigma$ transitions. In our opinion the latter is the more reasonable as it seems improbable that all the electron states of this molecule should be ${}^1\Pi$ states with no ${}^1\Sigma$ state present. For a final decision, however a more accurate study of the bands must be made, with plates of greater dispersion.

It has been shown in the preceding paper that the three known systems of the PbO molecule, A, B, and D, have the final state in common, hence we may reasonably assume that this state is the normal state of the molecule. The nuclear separation $r_0 = 1.9207 \times 10^{-8}$ cm., while larger than that of other oxides [10] so far investigated, is comparatively small for such a heavy molecule. This seems to indicate that the normal state is fairly stable.

If we assume that in the formation of PbO only the four electrons of Pb in the P shell are greatly influenced by the O atom, then the configuration of outer electrons in the PbO molecule should resemble that of CO with a ${}^1\Sigma$ state as the normal state of the molecule. It appears to us that the data on hand are neither sufficiently accurate nor extensive to warrant any further conclusions as to the electron states of PbO. The fine structure analysis of the bands is being continued in Ryerson laboratory, in order to determine this and other related points.

In conclusion the writers wish to acknowledge their indebtedness to Professor R. S. Mulliken, who proposed this problem, for his advice and many helpful suggestions.

[9] R. S. Mulliken, Phys. Rev. **29**, 391 (1927). See also Hönl and London, Zeits. f. Physik **33**, 803 (1925), for the derivation of these equations. The equations as given here are in terms of the final quantum number J.

[10] Compare CO, 1.15×10^{-8} cm, and TiO, 1.619×10^{-8} cm.

A LABORATORY METHOD OF PRODUCING HIGH POTENTIALS

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Abstract

Details are given of the experimental arrangement by which, using Tesla coils in oil, very high potentials have been produced and measured. Excited at the rate of 120 sparks per second Tesla coils have been operated at 3,000,000 volts in ordinary transformer oil at atmospheric pressure. In oil under a pressure of 500 pounds per square inch, voltages as high as 5,200,000 have been produced with intermittent excitation. These voltages (peak values) are measured by a simple capacity-potentiometer, in which an insulated electrode "picks up" a known fraction of the total voltage, this fractional voltage being measured by means of a sphere gap. Measurements are given of the voltage-distribution along Tesla coils. Calculations and measurements of the efficiency and power-output of such coils show that at 120 sparks per second, a coil operating at 5,000,000 volts provides sufficient power, if used to accelerate helium nuclei in a suitable vacuum-tube, to yield the equivalent of about 2,600 grams of radium.

THE importance of obtaining sources of high-speed electrons and atomic nuclei for physical investigations is so obvious that an explanation of the aim of the present work is hardly needed. It may be permitted however to say a few words about the part played by experiments with penetrating radiations in the past and to mention briefly some of the current problems for the solution of which the development of new and more powerful sources than have been available appears to be essential.

The Rutherford-Bohr atomic model was suggested by experiments on the scattering of α-particles. Their penetrating nature made it possible to obtain a simple interpretation of the results. The understanding of the nature of the solid state has received its main stimulus from experiments following Laue's discovery. Here the penetrating x-ray quanta offer direct and clear information; similarly with the Compton effect and with Rutherford's nuclear disintegration experiments. These very important experimental facts forming the foundation of modern theoretical conceptions have come out of experiments employing high-energy quanta, electrons, and α-particles. The historical reason for the importance of high-energy experiments is, of course, that classical physics corresponds to energy-jumps of zero-value so that the larger the energy concerned the more radical the departure from classical physics and the more interesting the phenomenon. Quantum mechanics has explained in recent years all of the fundamental facts in ordinary atomic structure. According to current theoretical opinion it is highly improbable that one shall find a serious contradiction to the present theoretical scheme by studies of line and band spectra. Apparently

the main unsolved questions at present are Dirac's $\pm m$ difficulty and the combined relativistic treatment of matter and electrodynamics. The first of these as shown by Klein becomes particularly pronounced for potential walls of high absolute value. It may be hoped that light may be thrown on the question by studies on nuclei by means of particles with high kinetic energy.

The precise form of the equation for one electron is intimately concerned with the $\pm m$ difficulty. It will be noted that by studying the intensity of scattering of recoil-electrons by hard γ-rays, Skobeltzin[1] has recently obtained evidence for preferring Dirac's equation for a free electron to the older Schroedinger form. His intensities agree with the calculations of Klein-Nishina, which use Dirac's equation, rather than with the older calculations of Dirac employing the Schroedinger equation without spin. It is not altogether clear at present to what extent Skobeltzin's experiments prove the validity of Dirac's equation or deal only with the presence of the electronic spin. It is clear however that when repeated with still more penetrating radiation they will give very important evidence. The practical approach to the combined treatment of matter and the electromagnetic field is also in all probability to be obtained by studying systems containing two particles in a state of rapid relative motion. Experiments on atomic nuclei giving their energy-levels, conditions for disintegration, etc., may be expected to offer new and valuable evidence for these still unsolved theoretical points and may besides suggest quite different questions and difficulties which do not come up in dealing with phenomena outside atomic nuclei.

We have thought it worth while therefore to construct high-potential equipment of convenient laboratory dimensions to make it possible to perform experiments on high-velocity particles. The electrical problem of producing high potentials was solved without much difficulty over two years ago.[2] The construction of high-potential vacuum (x-ray) tubes has proved more difficult but is at present sufficiently advanced to make a progress-report of interest and to show that the Tesla coils used for producing high potentials are suited for supplying the potentials to vacuum-tubes. The details of the electrical arrangement not having been published before we have divided the matter into two parts the present paper being concerned with the electrical arrangements and the one following with the construction and experiences with high-potential vacuum-tubes.

The apparatus used for producing high potentials is old and well-known under the name of Elihu Thomson or Tesla coils. Since their invention Tesla coils have been known to give possibilities of producing with limited means potentials of the order of one million volts.[3] They have commonly been used in air, the insulating qualities of which constituted a limitation on their performance. It is difficult to construct Tesla coils of sufficiently large dimensions to prevent corona and sparking in air. The energy con-

[1] D. Skobeltzin, Nature **123**, 411 (1929).
[2] G. Breit and M. A. Tuve, Nature **121**, 535 (1928).
[3] M. Wolfke, Phys. Zeits. **24**, 249 (1923).

sumed in the corona and sparking is so large that the Tesla coil ceases to operate as a resonance-transformer on account of the high damping and loses most of its advantages. If the dimensions of the coil are sufficiently large to prevent corona its electrostatic capacity becomes inconveniently large and necessitates unnecessarily cumbersome primary circuits. The main point in the operation of Tesla coils is therefore to prevent corona and sparking by using the high-potential parts of the coil in a medium of high dielectric strength. For a number of years two of us had in mind the possibility of using Tesla coils in a vacuum or in some other insulating medium. The method described here employs transformer oil which we have found sufficient for roughly five million volts when used under pressure and three million volts at atmospheric pressure. These figures are somewhat arbitrary, simply being the voltages obtained in the laboratory and not representing final limits in the voltages obtainable with oil. No doubt still higher voltages can be obtained by using oil for insulation. The practical advantages of oil over vacuum for preliminary trials are obvious when the question of repairs, changes in design, and baking out of metal parts is considered. The ultimate possibility of using Tesla coils in a vacuum is of course not excluded.

Experimental Arrangements

The principles underlying the operation of a Tesla coil are well known and need not be explained here in detail. The important thing is that two resonant oscillatory electrical circuits, the primary and the secondary, are coupled magnetically to each other. The primary circuit has a large capacity and a small inductance while the secondary (the Tesla coil) has a large inductance and a small capacity. The condenser of the primary circuit is charged to a high potential (of the order of 30 or 60 kv) and is allowed to discharge suddenly through a spark-gap and the primary inductance. An oscillatory discharge takes place. The secondary circuit being in resonance with the primary the energy is transferred with fair efficiency to the secondary before the damping appreciably reduces the amplitudes of oscillation. In the set-ups used the peak-voltage of the secondary circuit corresponds roughly to the transfer of one-fourth of the energy of the primary condenser to the secondary. The resonant frequencies of the coils used have been of the order of 100,000 cycles per second.

Figure 1 shows the arrangement for a Tesla coil in oil under pressure, with which over 5,000,000 volts were obtained. The condenser is fed on rectified current supplied by an x-ray machine. The primary gap is of the stationary type.* The use of rectified current is advisable if power consumption and large charging currents of the primary condenser are to be avoided. The arrangement can also be used without a rectifier, the primary condenser being then fed by a transformer and discharged through a syn-

* It can be made cheaply out of ten-inch hollow zinc-balls used for decoration purposes and usually furnished in the form of two hemispheres. For long and continued use heavier electrodes are preferable.

chronous gap. For our highest voltages we have been forced to use the rectifier because our power-lines have the unusually small capacity of 50 KVA.

The synchronous gap has been used up to 3,000,000 volts secondary output. The transformer was fed on 60-cycle alternating current and the condenser was discharged 120 times per second. No pressure had to be applied to the oil for this voltage. Even at low voltages, however, we find it convenient to use the rectifier when possible because by so doing a weak spot in the insulation of the secondary can be detected before electrical breakdown causes too much damage. In our experiments with oil at atmospheric pressure, corona at the ends of the Tesla coil limited the voltage obtainable to about 3,000,000. With the high-pressure arrangement corona has not given any serious difficulty. Insulation between turns limited the voltage in this case to about 5,000,000 volts.

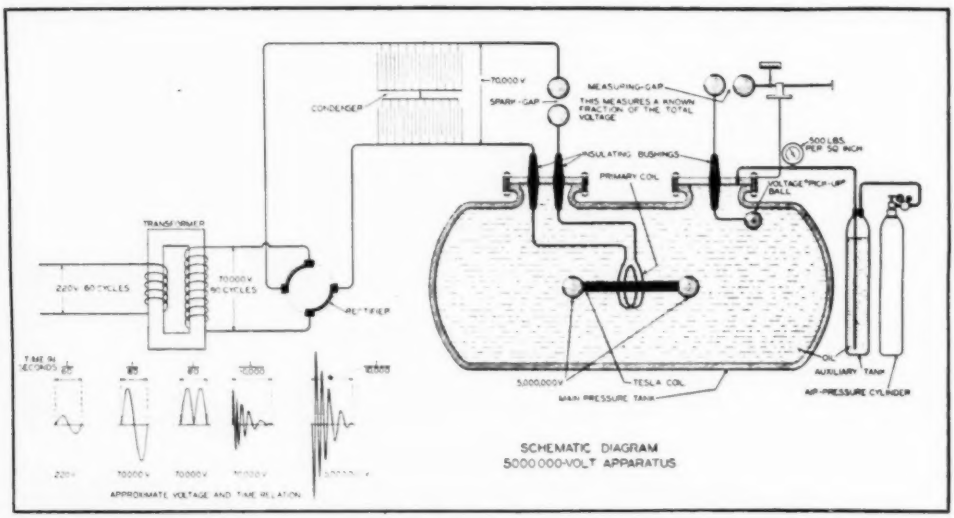

Fig. 1. Schematic diagram Tesla coil in oil under pressure.

Power-supply for the primary condenser.—For the production of 3,000,000 volts we used a small transformer giving about 30,000 volts and operating on 60 cycles with approximately a 3-kilowatt rating, kindly loaned to us by the Washington Navy Yard. For the intermittent production of the higher voltages we used a 10-KVA Kelley-Koett x-ray machine operating on a 220-volt 60-cycle supply. This or any other reliable x-ray machine contains the transformer mechanical rectifier and controls needed for charging the condenser. A potential of 120,000 volts could be supplied by the machine. In our experience we have rarely used it above 70,000 volts.

Condenser.—The work was begun by using a set of glass-in-oil Telefunken condensers loaned by the Washington Navy Yard; these had previously been used in a high power Navy spark-transmitter. Sixteen of these sufficed for the production of 3,000,000 volts. The capacity of each was 0.038 microfarad and each unit stood 15,000 volts (peak). For higher voltages however

we constructed a special condenser similar to that used by Anderson for exploding wires. Lead foil 0.003 inch thick was applied to each side of 200 glass plates. The plates are 40 inches square of somewhat irregular thickness approximating one-eighth inch, being ordinary B-grade double-strength window-glass. They are assembled in wooden racks in air and constitute a generally useful as well as comparatively inexpensive piece of laboratory equipment. Figure 2 shows a condenser including part of the lower and most

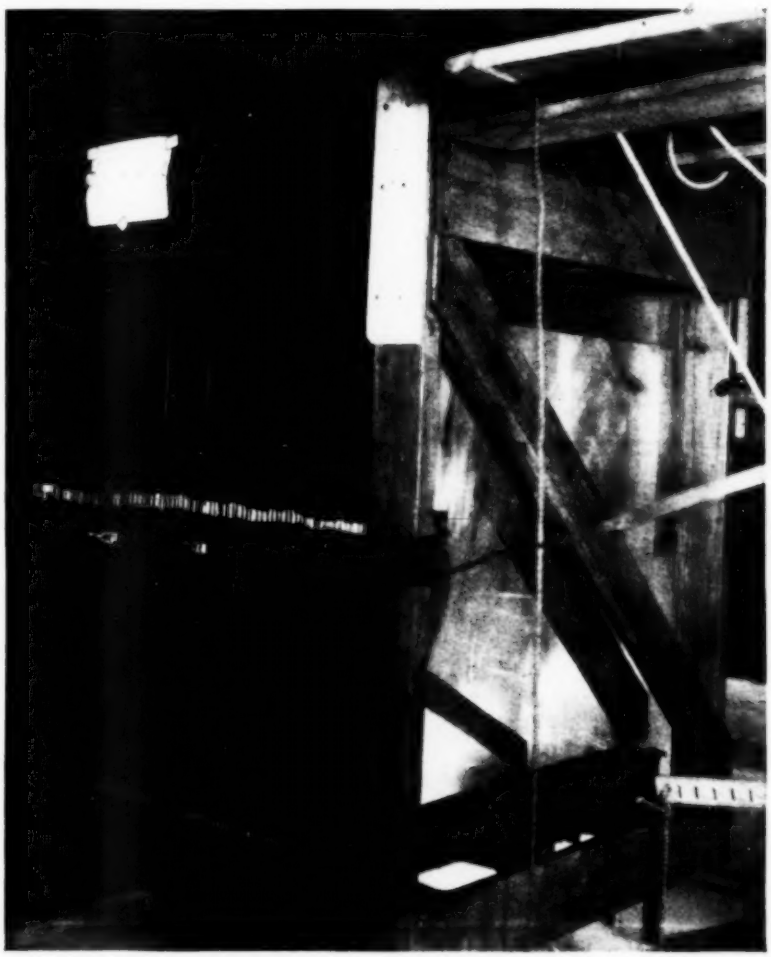

Fig. 2. View of section of the glass-plate condenser ($C = 1.6\mu$f, 30,000 volts).

of the upper rack. The plates are spaced one-half inch apart. For reasons which are somewhat obscure it is essential that the plates be spaced to prevent breakage when the condenser is discharged. We found it very convenient to fasten the lead foil to the plates simply by an oil-film. Any lubricating oil of a not too heavy consistency is satisfactory, but linseed oil seems to be the most convenient material for this purpose both on account of being easily squeezed into a thin film under the lead foil and because it dries around

the edges. A margin of about 4 inches is left on the glass around the foil, allowing the plates to go up to a sufficiently high potential and yet providing a safety-gap around the edge of the glass plate. In two years we have not had a single puncture of the plates although the condenser has been repeatedly at the flash-over point. In case of breakage however the plates can be taken out of the racks with relative ease. Pieces of rubber tubing inserted between plates close to the edges help to secure a uniform distance between them. The side of the racks shown in the figure is provided with two pieces of angle brass (only one is visible) which serve as supports for the connectors to the plates and as bus-bars. The opposite side (not shown in the figure) has each bus-bar split into two insulated sections thus allowing the use of the plates either all in parallel, in two sections in series, or in four sections in series. The capacity of all plates in parallel is about 1.6 microfarads. The maximum voltage which can be used with the plates in parallel varies between 30,000 and 40,000 volts depending on the type of external circuit. As a rule a high inductance in the external circuit allows one to use a

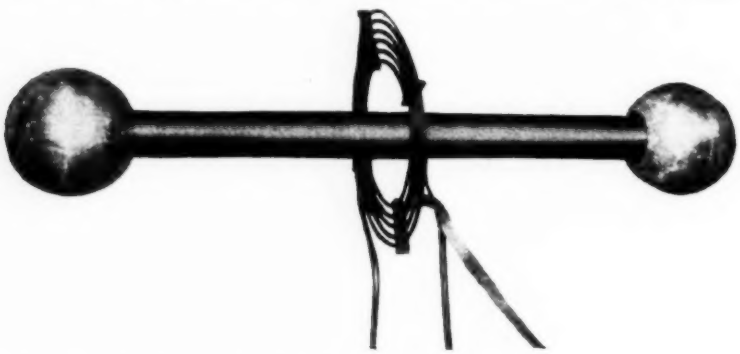

Fig. 3. Tesla coil and primary, showing the spun-zinc balls which serve as corona-shields at the ends of the Tesla coil.

higher voltage on the condenser. If the voltage exceeds this limit a local flash-over occurs around the edge of a plate when the primary gap discharges. The exact nature of the flash-over is hard to explain but it is undoubtedly due to transients. When it occurs the primary circuit becomes inefficient but in our experience no particular damage to the condenser takes place. With the four sections in series we have used this condenser without flash-over at 120,000 volts.

Primary of Tesla transformer.—This as shown in Figure 3 is made of several turns of spirally-wound copper tubing. Some of the most efficient circuits employ only two turns.

Tesla coil.—This is shown also in Figure 3. It is convenient to wind a high-voltage Tesla coil on a piece of Pyrex glass tubing as supplied by the Corning Glass Works with an approximate diameter of 8 cm and length of about one meter. The wire is generally wound without spacing and always in a single layer. The ends are protected by approximately spherical caps, those shown in the figure being 25 cm in diameter. When the Tesla coil is

immersed in oil it is important to eliminate the air which is likely to be trapped between the wires and the glass. If silk-covered wire is used soaking in oil is often sufficient to draw it in by capillary action. Vacuum impregnation is often advisable. For this purpose the coil is put in a tin tray and inserted into a horizontal piece of 6-inch pipe. The pipe is closed, exhausted, and oil is let in slowly with the vacuum-pump running. When the tray is full the pump is disconnected, the tray is taken out, and the coil is ready for use. Our best coils were made of No. 38 or No. 40 B.S. gauge copper wire, 5,000 to 7,000 turns. Either double silk, silk enamel, or the especially heavily enameled No. 40 wire (made by the General Electric Company) are satisfactory. It often happens that there are flaws in the insulation of the wire. These cause sparks between turns as soon as the coil is used and the coil is often burned out at such points. Having thus found out the weak points a few turns are unwound, the wire is scraped carefully at the ends, and is spliced; such a repaired coil is usually better than a fresh one. Insulation between turns usually gives no trouble up to 3,000,000 volts peak.

A screw is fixed permanently in the ball so that the ball can be screwed as a whole into a tapped hole in a brass end-piece fixed on the axis of the Tesla at its end. Incidentally, Houston's water putty made by the Gold Medal Polish Company (Racine, Wisconsin) provides a very convenient means for fastening attachments to Pyrex tubing. In most of our experiments the Tesla coil has been supported in the oil by a loop of silk fish-line at each end, which stands the full voltage to ground without trouble.

Oil and high-pressure tank.—Light transformer oil (not switch oil) purified by passing through a centrifuge has been used. Most of the oil employed by us has the trade name Transil 10 C. At its best clean oil is broken by about 46,000 volts across a 1-mm gap; in thicker layers its apparent dielectric strength is always less than this. The effective dielectric strength also depends to a large extent on the state of the electrodes between which the discharge takes place. No exact quantitative values can be assigned to it in our experience except by allowing a considerable safety-factor. It has proved possible to improve the performance of the oil by continued and judicious use. A preliminary discharge is often likely to take place while using a Tesla coil before the dielectric strength of pure oil is reached. We find it advantageous to "break in" the oil by allowing such discharges to occur. The procedure in this "breaking in" process is to bring up the Tesla voltage gradually. For very low voltages the caps on the ends of the coil show no discharge. As the voltage is brought up occasionally a corona "tree" shoots out from one of the caps into the oil. If the voltage is held at such a value that the "tree" occurs only seldom, the "trees" disappear after continued use. The voltage may then be brought up higher, "trees" occurring again occasionally and again disappearing after continued running. This process cannot be continued indefinitely but it is quite essential in improving the performance and obtaining as high a potential as possible. If the "trees" refuse to disappear it is often advisable to lower the potential to a point where they occur less frequently and to make them disappear

there. The "breaking in" of the oil and cap surface can be done either with a Tesla using 60-cycle excitation with a synchronous primary gap, or else by the intermittent primary sparks produced when using the x-ray machine. We have no special evidence of the superiority of either method. The synchronous gap is likely to shorten the time required but it is also likely to carbonize the oil if too heavy discharges occur. Its main danger lies in burning out the fine wire of the Tesla at points where the insulation on the wire is defective. We have obtained 3,000,000 volts with a Tesla used on 60-cycle synchronous gap excitation, the ends of the Tesla being protected by 5-inch spun copper caps. The mode of oscillation of the coil was such that the middle of it was at ground while the ends were at each instant at equal and opposite potentials. Each 5-inch cap was therefore at 1,500,000 volts corresponding to a gradient of 240,000 volts per cm. We did not find it practical to use much higher gradients in oil at atmospheric pressure, the performance of the apparatus becoming unreliable due to the corona from the caps. Also the apparent gradient to which the oil may be brought up depends on the caps used. An increase in the diameter of the caps makes it possible to bring them up to a somewhat higher potential. However the gain in potential is always less than would be calculated from the diameter. The exact reason for this we do not know but the obvious difficulty of having a perfectly shaped light metal sphere of large diameter, and of keeping it clean and polished, has probably much to do with it. The nature of the "breaking in" process we also do not know much about. It may be connected with removing dirt or microscopic particles of moisture from the electrodes or even with a local purification of the oil due to driving moisture or small air bubbles away from regions in which the electric field is large. Our main concern with regard to the production of high voltages has been the purely practical one of using oil at as high a value of the electric field as possible in order to test the voltage and power-output limitations of the method.

To improve the performance of the oil beyond that which was obtainable by ordinary purification and "breaking in" at atmospheric pressure we resorted to the pressure-method.[4] The pressure container is shown to scale in proportion to the Tesla coil in Figure 1. It is a hammer-welded iron tank originally made by the M. W. Kellogg Company of Jersey City for use as a steam separator. It is designed for a working pressure of 450 pounds per square inch in accordance with the standard boiler safety-code. [The importance of precautions in the use of high pressures in large containers cannot be over-emphasized.]

The tank was furnished with solid manhole plates which were later machined with proper openings for the insulating bushings and peep-holes (not shown in the figure). A peep-hole was put in each manhole plate. Each hole, three inches in diameter is covered with two-inch plate-glass. The inside of the tank was illuminated with two automobile headlights, current being supplied through an ordinary spark-plug screwed into a third manhole of the crab type in one head of the tank. This third manhole has been

[4] F. Koch, Elektr. Zeits. **36,** 85 and 99 (1915).

omitted in the figure. The pressure was applied to the oil by means of a carbon dioxide cylinder shown in the figure as "air-pressure cylinder." On account of the increase of volume of the tank under internal pressure and on account of the compressibility of the oil it is necessary to supply extra oil (several gallons) when pressure is applied. This is done by connecting the carbon dioxide pressure-cyclinder to the auxiliary oil tank shown in the figure.

The "breaking in" of the oil is essential also in this high-pressure arrangement. It is difficult to give exact figures for the improvement in the dielectric strength due to pressure. Roughly a factor of two is correct in our experience. The limitation which we encountered in the use of Tesla coils in oil under pressure was due to insulation between turns and not to "trees" (corona) off the caps. With longer Tesla coils it would be doubtless possible to exceed our voltages. The maximum which we obtained was 5,200,000 volts. The coil was wound with ordinary No. 40 enameled and silk-covered wire. The caps were 20 cm in diameter and the length of winding was approximately 90 cm. The mode of oscillation was again the half wave-length, that is, middle at ground and ends at opposite potentials. The application of pressure improves the insulation between turns as well as the insulation around the caps, there apparently always being a film of oil between turns. The improvement for the caps, however, proved to be so large that they offered no serious difficulty. The oil is purified at intervals by means of a Hydroil centrifugal purifier.

Measurement of high potentials.—We have used two methods of estimating the potentials. The first was used purely qualitatively although it can be developed into a quantitative one. It consisted in observing the deflection of a cathode-ray beam in a low voltage cathode-ray oscillograph. The latter was of the Johnson type made by the Western Electric Company giving cathode rays of 300-volt velocity observed visually on a fluorescent screen. The cathode-ray tube was put vertically in a wooden box the outside surface of which served as a support for a set of vertical grounded wires. These allowed only horizontal fields to affect the cathode rays. The sensitivity of the tube to electric fields inside the shield was determined experimentally by putting it in known fields produced by an electron-tube oscillator. One centimeter deflection on the screen could after the calibration be interpreted as a known electric field. When the cathode-ray box was put in the neighborhood of the Tesla coil the deflection on the screen was observed and the oscillating electric field due to the coil thus determined.[5] From a knowledge of the potential distribution on the coil and the distances involved the numerical value of the potential can be computed. The difficulty of this method lies in the extreme weakness of the trace on the fluorescent screen

[5] For this experiment the Tesla coil was supported in an open wooden tank containing the oil, although for experiments at atmospheric pressure we now use a 1500-gallon steel gasoline storage tank with about one-fourth of the cylindrical surface cut away. No particular loss of efficiency is occasioned by operating these high-frequency coils inside of a metal tank. This is clear, of course, from the results with the thick-walled high-pressure tank.

due to the extremely short duration of the high potential on the Tesla coil. The visibility of the trace being so low no quantitative measurements could be made. The estimates thus formed were checked however by measurements by the second method. Photographic registration of the cathode ray, as in the Dufour cathode-ray oscillograph, would make the first method quantitative and we mention it mainly for this reason.

The second method can be described as a capacity-potentiometer or "pick-up" measurement. The principle is shown in Figure 1. The manhole on the right of the high-pressure tank is provided with an insulating bushing which supports a voltage "pick-up" ball. Since the potential on the Tesla coil alternates with a high frequency (approximately 100,000 per second) the potential assumed by the pick-up ball is determined by the capacities between the Tesla coil and the ball as well as between the ball and the ground. In order to know the potential of the coil it is sufficient therefore to measure the potential on the "pick-up" system and to determine the ratio of the potential on the coil to the potential on the "pick-up." The measurement of the potential on the "pick-up" system is made by means of a sphere-gap and the ratio of the two potentials is determined at low voltages where the potential of the Tesla coil can be measured directly. The direct measurements of the Tesla-coil voltages in the low range have been made in two ways. The most direct method is to connect a sphere-gap across the coil. In doing this care is taken to have the high-potential lead to the sphere-gap removed as far as possible from the "pick-up" ball so as not to change the relative distribution of capacities. Since this can never be done perfectly, although in general it leads to underestimating the true voltage, we have also determined the potential ratio, or calibration-factor, by a somewhat different method free from this objection.

The second way of determining the calibration-factor makes use of the fact that the potential at the middle of the Tesla coil is the same as that of the ground, and that a small capacity around a small section of the coil at its middle does not change appreciably the voltage-distribution along the coil. Thus the coil is provided with taps exactly at the middle as well as at one and two centimeters to each side of the middle. The coil is excited by sustained oscillations from an electron-tube oscillator. A bifilar electrometer is connected across the middle tap and one of the others, and another bifilar electrometer is connected across the measuring gap. The ratio of the two measured potentials gives therefore the ratio of the potential across one centimeter of the Tesla coil at its middle to the "pick-up" potential. In order to determine the calibration-factor it is now only necessary to find the ratio of the potential across the whole Tesla coil to the potential across a centimeter of it at its middle. This was determined by finding the potential distribution along the coil by special experiments.

It may be shown by calculation that the change in the resonant frequency of a Tesla coil when a capacity is connected across a section of it is proportional to this capacity and the square of the voltage across the section in question. This calculation presupposes that the change of frequency dealt

with is small. Model Tesla coils were built with taps and the "detuning" effects were observed when a small fixed condenser was connected across the various sections. The square roots of the detuning effects $(\Delta C)^{1/2}$, when ΔC is the capacity-change required to retune an oscillator coupled to the Tesla coil, gave the potentials across the separate sections and hence by addition the potential distribution along the coil. The magnitude of the fixed capacity used was varied so as to make sure that it was small enough and not sufficient to cause partial resonance of a part of the coil which would vitiate the measurements. The condenser employed to produce the capacity-changes was made of two circular plates about 5 cm in diameter separated by a thin sheet of mica and thus had a fairly small capacity to ground. This capacity was sufficient to require a correction because it was found that if the condenser was connected to one of the taps it had a measurable detuning effect on the Tesla coil. This detuning effect was therefore ascertained for all the

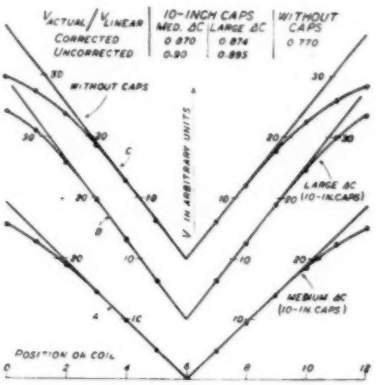

Fig. 4. Voltage-distribution curves for Tesla coils (points are plotted for corrected data only; the uncorrected points are almost indistinguishable from these on the scale of the figure).

taps and corrected for by subtracting it from the detuning effect of connecting the condenser across two adjacent taps. The remaining number gave the detuning due to a capacity across the two taps without having a capacity to ground. This correction reduced the resulting form-factor only two or three percent, however, (see Figure 4). When different condensers were used the voltage-distribution curves corrected for the capacity to ground of the "probing condenser" checked closely for different capacities of the condenser used. Such measurements were made on Tesla coils wound with different sizes of wire and with different caps on the ends. The voltage-distribution curves proved to be independent of the size of wire used for winding the Tesla coil. Experiment shows however that it depends appreciably on the capacity load at the ends and that it is different for different sizes of caps used. The results can be expressed most conveniently in terms of the ratio of the average slope of the voltage-length curve to the maximum slope at the middle of the coil. For coils of the dimensions used by us this ratio or "form-factor"

is 0.77 for coils without caps (Figure 4C), 0.82 for 5-inch cast bronze caps, 0.87 for 10-inch caps. The voltage-distribution thus becomes more linear as the capacity-load at the ends is increased, as would be expected. Knowing the "form-factor" of the coil we obtain the potential across the coil from the potential across one centimeter of it at the middle by multiplying the latter potential by the length of the coil in centimeters and by the "form-factor."

We have ascertained the effects of the capacity of the electrometers used in the measurements by connecting a third electrometer either at the measuring sphere-gap or at the tap across the middle of the Tesla coil. These effects are small and corrected for. The calibrating-factors obtained by the first or second method of measuring the Tesla-coil voltage agree very closely. In both cases we also have made sure that the "pick-up" voltage is due to the potential on the Tesla coil itself rather than to induction from the primary and calibrating circuits by partially or completely detuning the primary circuits from the Tesla coil. This reduces the "pick-up" voltage to zero.

Every calibrating-factor depends on the setting of the measuring gap because the capacity of the "pick-up" system to ground is affected by the distance between the two measuring spheres. A curve for the calibrating-factor against the "pick-up" gap setting is plotted and used in the calculation of the voltage. The corrections due to this cause are of the order of 5 to 10 percent in our set-ups. The measurement of the "pick-up" voltage in actual operation consists in determining the separation between the spheres at which sparks definitely pass between them. The potential across the gap is then obtained from the data of Peek.[6] The potentials of the secondary gap are generally of the order of from 30,000 to 100,000 volts thus allowing one to make fairly accurate gap-settings. Since voltage-measurements by a sphere-gap may be subject to corrections due to local conditions such as air ionization, surface condition of gap, etc., as a precaution we have checked one of our gaps on 60 cycles against an electrostatic voltmeter and found the results to be in agreement with Peek's data. For our measuring gaps we always employ 25-cm (10-inch) diameter spheres, which are known from the work of Peek to be reliable indicators in the range of voltages used. A sphere-gap does not give as consistent readings immediately after polishing as it does after a number of sparks have passed. Freshly polished spheres will spark occasionally at a greater separation than will "used" spheres for a given voltage. We have always taken measurements with gaps in the "used" condition, leading to lower rather than higher voltage-estimates.

It may be observed that if the oil should become partially conducting under the influence of high electric fields the "pick-up" method would be seriously vitiated and would tend to give exaggerated values to the Tesla voltage. We have taken care therefore to make sure that this is not the case.

[6] F. W. Peek, Jr. Dielectric phenomena in high-voltage engineering (McGraw-Hill, 1920) Chapter IV; Trans. A. I. E. E. **34,** 1857 (1915); J. Franklin Inst. **197,** 1 (1924) and **199,** 141 (1925); Smithsonian Inst. Report for 1925, 169 (1926). Also L. W. Chubb and C. Fortescue, Proc. A. I. E. E. **32,** 627 (1913).

Our main evidence lies in the fact that the measured Tesla voltages, with a given primary setting, are independent of the position of the "pick-up" (each position of course being separately calibrated at low voltage) as long as there are no "trees" from the caps in the oil. Since at low voltages used in the electrometer-calibrations there is absolutely no possibility of a non-uniform oil-conductivity we conclude that the oil-conductivity is uniform also when high potentials are used unless a visible breakdown occurs as shown by "trees" or bolts in the oil. In the second place we find that the measured Tesla-coil voltage is proportional to the potential to which the primary condenser is charged which is determined by the setting of the primary gap. This again would not be the case if the conductivity of oil and invisible discharges played any part in the measurements. If insufficient care is exercised in preventing corona in air or the discharges along the surface of the oil from the high-potential connections of the measuring gap, too low values of the Tesla voltage may result. The only deviations from linearity which we have observed have been due to these causes.

Data on the efficiency of Tesla coils.—We have made rough measurements of the potentials developed by Tesla coils with various sizes of caps in terms of the potential of the primary gap. The measurements given in the table were all made with a primary voltage of 6500 and with half wave-length excitation of the Tesla coil. V_T represents the total voltage between caps, measured by the capacity-potentiometer method. Each cap is therefore charged to a voltage $V_T/2$ above ground. The primary circuits and the coils may be rated either from the point of view of having a certain maximum usable primary potential or else on the basis of having a certain maximum number of plates for the primary condenser. For this reason we tabulate both the ratio V_T/V_P giving the voltage gain-factor of the Tesla over the primary and applying therefore to the case when the primary potential is the limitation, and also $C_P V_P^2/V_T^2$ expressed in micro-microfarads. The latter figure gives the effective capacity of the Tesla coil which for this purpose is defined to be such a capacity C_T which would attain a voltage V_T if all of the energy $C_P V_P^2/2$ of the primary condenser were transferred to the capacity C_T. The point is that a given number of plates available for the primary condenser whether used all in parallel or in several groups in series gives roughly the same maximum value of $C_P V_P^2$ and therefore if the limitation lies in the primary condenser a small value of $C_P V_P^2/V_T^2$ is an advantage.

It is seen from the table that if the primary voltage is fixed a small primary inductance and a large primary condenser constitute the best circuit. If however the number of glass plates available for the condenser is limited it is perhaps at times better to use a reasonably large number of primary turns and therefore less primary capacity but a higher voltage by subdividing the condenser into sections used in series. A too large number of sections in series is of course not practical, leading to overvoltages and increase of circuit-inductance. A too small primary inductance however is also frequently harmful, leading to explosion-like flash-overs of the con-

denser. The use of the table is therefore only to select rough values for the circuit-constants. The best arrangement is found afterwards by trial. The table applies to the particular circuits which were made up of the Telefunken condensers and therefore takes account of the particular lead-inductances used with them.

The table shows the relatively high energy efficiency of the Tesla coil, which is capable of storing in its very small capacity about one-fourth of the energy of the primary circuit. This is made clear by comparison of the

TABLE I. *Data on efficiency of Tesla coils.*

Caps	Primary turns	Primary capacity in micro-farads	Transformation ratio V_T/V_P	$C_P V^2_P V^2_T$ in micro-microfarads
	No. 36 double silk-covered wire			
5-inch	2	0.19	101	19
	3	.13	85	18
6-inch	2	.26	104	24
	3	.16	106	14
8-inch	2	.33	106	29
	3	.22	99	22
	4	.15	83	22
10-inch	2	.41	121	28
	3	.30	112	23
	4	.20	94	23
	No. 40 General Electric enameled wire			
5-inch	3	0.45	162	17
	4	.33	147	15
	5	.23	115	17
	6	.19	87	25
6-inch	4	.48	123	32
	5	.37	113	29
	6	.27	97	29
8-inch	4	.60	131	35
	5	.45	118	32
	6	.33	107	29
10-inch	5	.54	137	29
	6	.45	119	32

last column of the table with the calculated capacities of the caps (remembering that each cap is charged only to $V_T/2$ above ground). Now a capacity of 1.5 microfarads at 30,000 volts contains 675 joules so that 170 joules can be put into the capacity of the Tesla coil. Even if it should be dissipated in one ten-thousandth second (about 10 cycles at a frequency of 10^5) this gives an instantaneous power of 1.7×10^3 kilowatts. By direct tests we find that a Tesla coil is able to feed about 20 megohms without having its voltage decreased to less than about half. Since insulation, rather than electrical efficiency, is the limiting factor at high voltages, the voltage under load may

be brought up to that obtained without load by supplying extra power in the primary circuit. At 5,000,000 volts the power-consumption through 20 megohms is 1.2×10^{3} kilowatts. The instantaneous power available in a Tesla coil is therefore of the order of one thousand kilowatts and at the high potentials produced the coil is capable of delivering fairly efficiently an instantaneous current of 5×10^{6} volts/2×10^{7} ohms$=0.25$ ampere. If now the coil is used on 60-cycle current, that is, with 120 primary sparks a second, and if only 10^{-6} second during each discharge (roughly one tenth of a cycle) is counted as effective in feeding a high-potential x-ray tube, the average current is $120\times10^{-6}\times0.25$ ampere$=3\times10^{-5}$ ampere. If only one spark a second is used an average current of 2.5×10^{-7} ampere can be drawn. The synchronous-gap excitation thus gives 1.9×10^{14} five-million-volt electrons per second and the one spark-a-second excitation gives 1.5×10^{12} electrons. For comparison with radioactive sources we recall that the number of α-particles emitted by a gram of radium per second is about 3.5×10^{10}. Thus at 5,000,000 volts one spark a second has sufficient power to drive 0.75×10^{12} α-particles equivalent to 21 grams of radium, and 120 sparks a second would be equivalent to 2600 grams. Such α-particles would have an energy of 10,000,000 electron volts, at least 2,000,000 volts higher than the highest energy α-particles obtainable from radioactive sources. We may conclude therefore that the amount of energy which may be drawn from Tesla coils is sufficient to obtain sufficient numbers of high-velocity particles for disintegration-experiments.

We are greatly indebted to Lieutenant William Klaus formerly of the Washington Navy Yard for arranging the loan of the apparatus with which this work was begun and to the Potomac Electric Power Company for a temporary loan of 400 gallons of transformer oil. Our particular thanks are due to our colleague, J. A. Fleming, for his energetic support and to B. Howard Griswold of Alexander Brown and Sons, Baltimore, Maryland, for temporary financial assistance.

THE APPLICATION OF HIGH POTENTIALS TO VACUUM-TUBES

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(Received November 22, 1929)

Abstract

A brief progress-report is made on the results so far obtained in the development of vacuum-tubes to which the very high voltages produced by Tesla coils (greater than 10^6 volts) can be applied. One cascade tube has been constructed which withstood repeatedly a voltage of 1,400,000 volts, and others have been used at lower voltages. This method, originally developed by Coolidge, gives promise of being suitable for voltages of several million, and eventually perhaps even higher. No effort has been made so far to use these tubes with a definite and controlled emission, since experience has shown that single-section tubes operated at several hundred kilovolts have approximately the same voltage-limitation with or without hot cathodes. The chief difficulty with very high-voltage tubes is that of preventing the uncontrollable (cold-cathode) emission which limits the voltage which can be applied. An electrodeless tube which withstood 1,000,000 volts is briefly described.

THIS paper is a brief progress-report giving some of our experiences and the results so far obtained in the development of vacuum-tubes to withstand the high voltages so readily produced by means of Tesla coils. Many different designs of tubes have been constructed, with different kinds of electrodes and variations in vacuum technique, and in general our conclusions parallel those of others working on similar problems using other high-voltage sources. It is very difficult to apply more than 300 to 400 kilovolts to a single two-electrode tube, whatever the design or treatment within practical limits. The reason for this is not known exactly at present. The main difficulties are presumably uncontrollable emission and accumulation of charges on the glass walls resulting in punctures and short-circuiting of the voltage source. We have succeeded, however, in applying Tesla voltages of considerable magnitude to vacuum-tubes by two methods, and these results seem interesting enough to merit a brief description.

(1). *The cascade-tube method*—This is essentially the method developed by Coolidge.[1] We have found it possible to use much smaller tubes for the same voltages by immersing them in oil. Figure 1 shows a picture of a 6-section tube used successfully at 850,000 volts. The overall length is 34 inches; the bulbs are of 100-cc size. A tube of similar design with fifteen 300-cc bulbs and having an overall length of 7 feet has gone up repeatedly to 1,400,000 volts. This tube is shown in Figures 2 and 3. Such tubes are at present always used by us on the pumps. The pump system is an ordinary diffusion or Langmuir pump arrangement. The electrodes are copper tubes

[1] W. D. Coolidge, J. Frank. Inst. **202**, 693 (1926).

with rounded ends of as large a radius of curvature as possible, the electrodes being rounded by "spinning" the ends in. We have used Pyrex glass for these tubes for mechanical reasons, although it is quite possible that other glass may prove more advantageous. We have preferred to use each section at a somewhat smaller voltage and to increase the number of

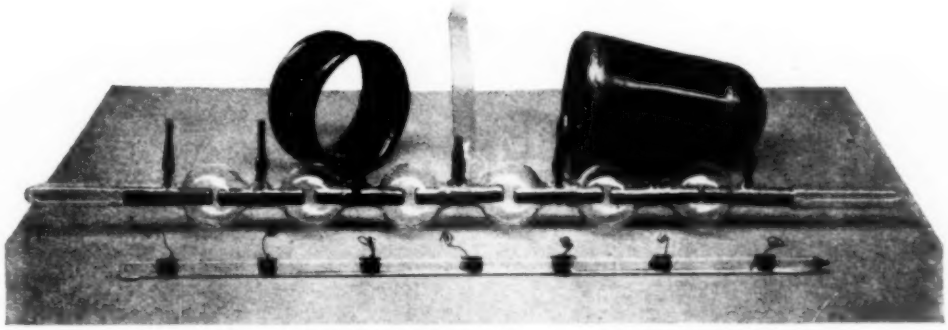

Fig. 1. Six-section tube, with potentiometer and typical shields unmounted.

sections rather than to design each section for operation at the limiting value of 250 or 300 kilovolts, although this no doubt can be done later even with small sections such as we are using. The essential points in the design of tubes are: (*a*) the subdivision of the whole tube into sections; (*b*) the uni-

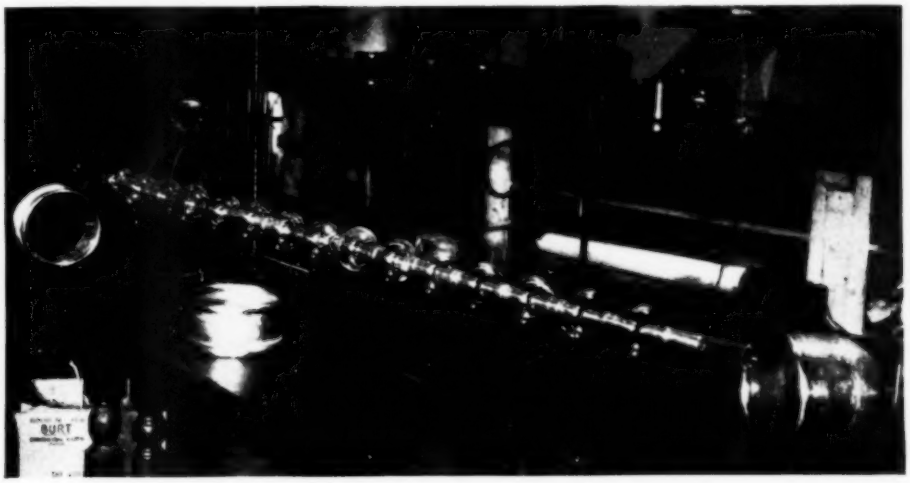

Fig. 2. Fifteen-section tube.

form distribution of voltage between sections by means of a potentiometer or some other electrical circuit; and (*c*) electrostatic shielding of the sections outside of the vacuum. The type of potentiometer used is shown in Figure 1. The glass tube is filled with a weak solution of salt in water. The concentration of salt is adjusted by trial until the potentiometer connected

across the Tesla coil produces a measurable effect on the voltage, for example until it reduces the total voltage by one quarter or somewhat more. The taps of the potentiometer are connected to the successive electrodes of the vacuum-tubes. In operation the potentiometer is put inside the shields.

The type of shield used is also shown in Figures 1, 2, and 3. The 15-section tube, each section of which was 4-3/4 inches long, had shields 3-3/4 inches long, the diameter of each shield being about 8 inches. The spacing between shields was about 1 inch. Experience showed that shielding of bulbs at high potentials is quite necessary. This may apply only to the high-frequency alternating type of potential we are using.

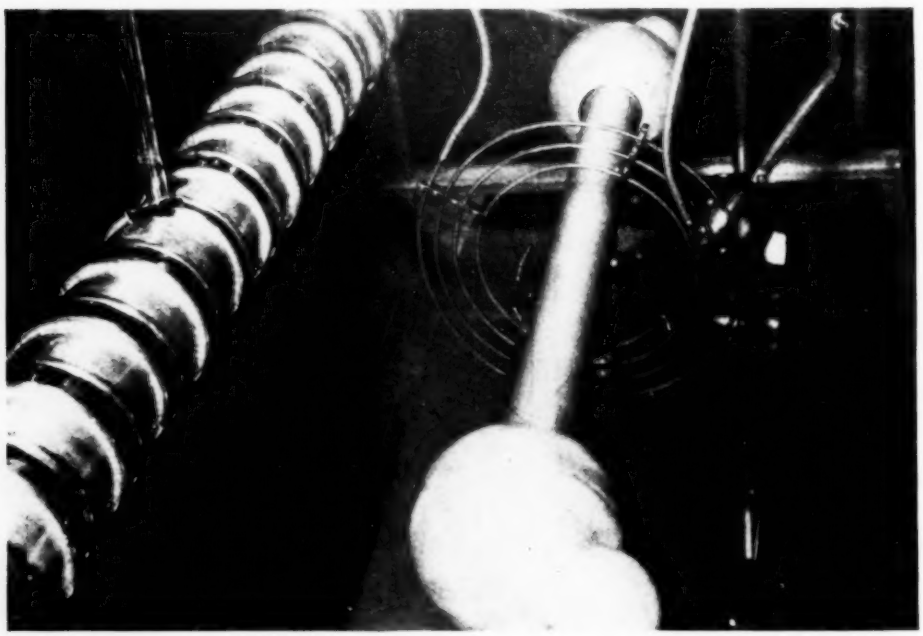

Fig. 3. Fifteen-section tube mounted in steel tank showing shields in position; Tesla coil in place but oil pumped out.

As is seen in Figure 1 the connections to the electrodes were made through waxed joints. There was thus no question of an extremely high vacuum since the tube as a whole could not be baked. The electrodes themselves (copper) were prebaked at 950°C in a quartz-tube furnace. The tube was also torched with a gas flame while evacuated, before the electrodes were put in. Carbon-dioxide snow in alcohol was used on the trap for keeping down the pressure of Hg and other condensible vapors. No refrigerant was used during the first half-hour of pumping, in order to pump out most of the water-vapor. Liquid air on the trap obviously might be quite dangerous in case of an accident, since the tubes are tested under oil. As indicative of the rather low degree of vacuum required it may be of interest to mention that the 15-section tube withstood 1,000,000 volts without trouble only 4 hours after

it was assembled and the pumps started. This was without torching any of the glass parts.

An important point about bringing up a tube to a high voltage is "breaking in" as in the case of x-ray tubes on direct current or low-frequency alternating current. When a potential is first applied the tube may flash at one-half of the potential which it stands without puncture after it is broken in. Our procedure is to bring the potential up cautiously until the tube flashes. Then the potential is lowered until the flashing weakens appreciably. After a few minutes running or less the flashing disappears. The potential is brought up until the tube flashes again and the procedure is repeated. In cases where one of a set of bulbs shows bad flashing it is sometimes helpful to break this section in by itself. There is of course an approximate limit which a given size of bulb of a given design will not exceed. The potential which can be applied to the whole tube is however rather accurately equal to the potentials which may be applied to the bulbs separately. Thus the bulbs act independently. The "breaking in" procedure may at times be carried out safely by letting the tube flash and allowing it to rest for a minute or two. Then the potential is applied again. The flash is often weaker or absent. It seems that it is important to pump off the gases evolved during a flash. The "breaking in" of a tube is somewhat similar to the "breaking in"of oil described in the preceding article. The "breaking in" lasts, that is, if a tube is broken in one day it can be broken in to the same voltage on the next day in a much shorter time. At times no "breaking in" the next day is required. In all of these experiments we use the intermittent voltage-excitation by means of a stationary primary gap and direct current on the primary condenser described in the preceding article. It may be that the same tubes would be subjected to more danger if used on other and more continuous sources of potential.

It will be noticed that the increase in the potential applied to the 15-section tube over that used on the earlier 6-section one was not proportional to the number of sections and was especially out of proportion to the total lengths. It might be supposed that the use of tubes with many sections is disadvantageous. No such limitation was responsible for the insufficiently high voltage applied to the larger tube. One of the shields which was insufficiently well supported, fell on the tube and caused a puncture at the point of contact with the glass during the "breaking in" process. The flashing at 1,400,000 volts was not due to lack of additivity in the action of the bulbs, because the bulbs when tried separately flashed at about 100,000 volts per bulb. This relatively bad performance of the bulbs was in all probability due to partial contamination of the electrodes with mercury which occurred during an accident to the tube. The amount of work involved in taking the electrodes out, baking them, and putting them in again being considerable, the tube was repaired without removing the electrodes. Since the electrodes in the 15-section tube were larger and more nicely rounded than in the 6-section tube and since the bulbs in it were also larger there is every reason to expect at least one-sixth of 850,000 volts per section when care is taken

to have uncontaminated electrodes. It must also be mentioned that one of the 15 sections was not used because of a defect in the potentiometer at that section. The additivity of potentials which may be applied to the bulbs separately when they are connected in series seems thus to be demonstrated. We expect therefore that a 2,000-kilovolt tube can be constructed without serious difficulty.

So far we have tried hot cathodes in single-section rather than cascade tubes. The puncture-voltage was independent of whether a hot cathode was used or not. The evidence is that its use will not make the operation on the cascade principle more difficult.

(2) *Electrodeless tubes*—These have been mentioned by us in a previous publication.[2] Under proper conditions a spherical Pyrex bulb immersed in oil between electrodes does not puncture when a million volts is applied to the electrodes. The arrangement is shown in Figure 4. The exact conditions for successful operation of such bulbs are still not certain. The evidence

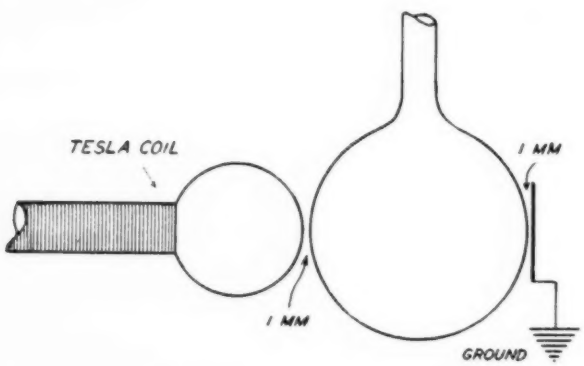

Fig. 4. Diagrammatic sketch showing the arrangement for electrodeless tube.

seems to be however that a partially electrically conducting-layer on the inside surface of the glass, in our case due to carbonized oil, is essential. The fluorescence patches of long duration observed with this type of bulb are quite similar to those occurring with the cascade-bulbs.

(3) *Miscellaneous experience*—Long tubes, with one electrode at each end put inside the Tesla, puncture readily. The high-frequency field produced by the Tesla is thus insufficient to prevent accumulation of charges inside the tube.

Sealed off commercial Coolidge tubes at times stand a higher Tesla voltage than would be expected from their behavior on direct current. This however is not always true. It was impossible in our experience to exceed 400 kilovolts without bad flashing. One 220-kilovolt deep therapy tube was punctured at 400 kilovolts.

An extraordinarily good vacuum is not essential in securing good operation of single-section tubes up to say 300,000 volts. Extreme precautions

[2] G. Breit and M. A. Tuve, Nature **121**, 535 (1928).

with regard to vacuum technique do not suffice in our experience to bring about anything but very erratic improvements beyond this figure.

One quite definite type of failure is that shown by "straight" tubes, whether single or cascade, made by enclosing the electrodes in ordinary drawn Pyrex tubing of a diameter not much larger than that of the electrodes themselves, instead of in bulbs. Such a rigid design of tube would be mechanically very desirable, but 10-section and 20-section tubes made in this way have failed well under 500,000 volts, the glass wall shattering inward from longitudinal striae or bubbles in the glass without puncturing through to the outside. Violent flashing then limits the voltage which can be applied. The striae are usually invisible before the shattering takes place.

The authors take pleasure in recording their indebtedness to O. Dahl, whose assistance during a part of this tube-work has been invaluable, and again to J. A. Fleming for his support of the work.

ANODE SPOTS AND THEIR RELATIONS TO THE ABSORPTION AND EMISSION OF GASES BY THE ELECTRODES OF A GEISSLER DISCHARGE

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Abstract

In a Geissler discharge containing H_2, N_2, CO, mixtures of hydrogen and the rare gases or mixtures of mercury vapor in the rare gases at pressures of 0.5 to 12 mm and electrode separation of 4 to 30 cm, the anode glow breaks up into a number of bright hemispherical spots, more or less symmetrically arranged when the polarity of a direct current discharge is reversed. Anode spots do not form in O_2, A or Ne but faint spots form in He which contain a trace of H_2. It is shown that one necessary condition for the formation of spots is the emission of gas from the surface of the anode. As many as 75 spots arranged in 5 concentric rings have been observed on an anode 34 mm in diameter. Conditions governing the number, size and duration of the spots have been determined. Spots formed on all the metals tried; Fe, Ni, Al, Cu, Hg and brass. The formation of anode spots has been used to prove that in a Geissler discharge between cold electrodes, the cathode absorbs gas and the anode emits gas at rates which are functions of the current density, gas pressure, kind of gas and electrode temperature. It is shown that the increase of the potential drop of a discharge with time, is due almost wholly to an increase in the gas content of the cathode, and that the potential drop immediately after starting a discharge is lowered by previously degassing the cathode by means of an induction furnace or by using this electrode as anode.

Introduction

ALTHOUGH hundreds of investigations have been carried out during the past fifty years on some part or other of the Geissler discharge, a complete understanding of the phenomena which occur therein is still lacking. Among these phenomena is the "clean up" or disappearance of the gas. It has long since been postulated that the electrodes absorb gas but in the past no direct proof of this has been given although the several explanations[1,2,3,4] of the phenomena of cathode sputtering have as their bases the absorption of gas by the cathode or the existance of gas in it.

That certain gases diffuse through certain metals is shown by the diffusion of hydrogen through palladium. Yamada[5] has shown by spectroscopic analysis that absorption of hydrogen in palladium produced a uniform expansion of the space lattices by 2.9 percent. He found no evidence that the absorbed hydrogen had reacted with the palladium.

[1] Hittorf, Wied. Ann. **21,** 126 (1884).
[2] Kingdon and Langmuir, Phys. Rev. **22,** 148 (1922).
[3] Berliner, Weid. Ann. **33,** 291 (1888).
[4] Kohlschutter, Jahrb. d. Radioakt. **4,** 353 (1912).
[5] Yamada, Phil. Mag. **45,** 241 (1923).

Baum[6] has made microphotographs of silver cathodes which had been used in a Geissler discharge of 3000 volts in which he found that gas molecules had penetrated to a depth of 1.5 mm.

In some recent experiments, one of the writers has had occasion to investigate an alternating current Geissler discharge in hydrogen. He found that during one half of the cycle of alternating current the discharge did not strike. During the succeeding half cycle, the discharge struck when the voltage had attained the sparking potential of the gas for the existing pressure-distance conditions. A check on the history of these electrodes showed that they were of the same metal and that they had been subjected to the same treatment except that a direct current discharge in hydrogen had previously been passed between them. The discharge struck with A.C. when the electrode previously used as anode in the D.C. discharge was negative.

This experiment shows that the use of an electrode as anode or cathode changes its sparking potential. Later in this paper, it will be shown that this difference in sparking potential was due mainly to a difference in the amounts of gas absorbed in each electrode. During the investigation of this difference in sparking potential, the anode spots appeared. The term anode spots is used throughout this paper to apply to the hemispherical bright spots which were more or less symmetrically arranged on the cathode side of the anode.

The appearance of anode spots has been previously reported by Lehmann[7] who found them in a discharge in air in a tube of wide diameter, and by Mackay[8] who found more elaborate patterns in helium. Neither author attempted any explanation of the formation of the anode spots.

Object

In the light of this information, it seemed advisable to make the following investigations: (1) A determination of the cause of anode spots; (2) A study of their characteristics; (3) An application of the phenomenon of anode spots to the study of emission and absorption of gases by the electrodes of a Geissler discharge; (4) A study of the effect of gas absorbed in the electrodes on the potential drop of the discharge.

Apparatus

The vacuum system consisted of the usual pumps, mercury cut-off and liquid air trap. The gas pressure in the system was determined by means of two McLeod gauges whose combined range extended from 30 mm to 2×10^{-5} mm of mercury. A gas storage and purifying system was connected by suitable stopcocks to the vacuum system so that either all parts could be evacuated to a high degree or purified gas could be admitted to the experimental tube.

Figure 1 is a diagram of the experimental tube most used. The tube proper was 63 cm in length and 6 cm in diameter. Electrical connections were made

[6] Baum, Zeits. f. Physik **40,** 690 (1926).
[7] Lehmann, Ann. d. Physik **7,** 8 (1902).
[8] Mackay, Phys. Rev. **15,** 309 (1920).

to the movable electrode through a capillary glass tubing which supported it. By means of a magnetic force on a cylinder of soft iron which was fastened to this capillary shaft, the one electrode could be moved through a distance of 30 cm. The electromagnet for moving this electrode was mounted on a screw device which permitted a slow regular movement of the electrode.

Electrodes of several sizes, shapes and thicknesses were used as well as similar electrodes with different degrees of polish. In several cases, extreme care was taken that no foreign material touched the electrode surface except the steel tool with which it was turned down. The electrodes were supported on glass stoppers in such a way that only one half inch of metal was exposed behind each electrode. Thus the distortion of the electric field was reduced to a minimum. The glass stoppers were ground to fit another tube of the same length as the first but of a diameter 4 cm larger than the latter. A third glass stopper which supported a spiral tungsten filament was interchangeable with the stopper which carried the fixed cold electrode.

A direct current motor-generator set supplied the potential which was regulated by changing the resistance in the circuit of the field exciter. The voltage across the tube was measured on a Jewell voltmeter of range 0 to 500

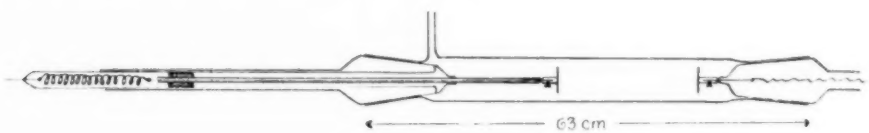

Fig. 1. Experimental tube.

volts. This voltmeter was equipped with suitable external resistances by means of which the voltage range could be extended up to 2000 volts. A resistance of 3000 ohms was placed in series with the experimental tube. By means of a reversing switch the direction of the discharge through the experimental tube was easily changed.

Procedure

Whenever any appreciable sputtered material appeared on the inner walls of the tube or when a change of electrodes was made, the tube was disassembled and cleaned with aqua regia. Subsequently, the tube was mounted in its usual position and the glass stoppers were turned until the electrodes were parallel and symmetrically placed as judged by the eye after which the ground glass joints were sealed with De Khotinsky cement. The necessary precautions were taken for the removal of water vapor and occluded gases and for the exclusion of mercury vapor from the tube.

Extreme care was exercised in order to obtain pure hydrogen, carbon monoxide, argon, neon and helium. However, in no case was it possible to remove all traces of hydrogen from helium, possibly because the system and tube had previously been used for hydrogen.

The electrode separation was determined by measuring the relative position of the soft iron cylinder on the shaft which supported the movable

electrode. By this method the electrode separation could be easily determined within one half a mm regardless of the condition of the discharge tube proper.

When the gas, tube, and electrodes were properly prepared, the gas was admitted slowly to the tube through a liquid air trap until the desired pressure was attained. In the cases in which the effects of complete degasification of electrodes were investigated, the discharge was set up in the tube within a few seconds after the gas was admitted to the tube in order that the electrodes might have little time for absorption of the gas.

The ordinary procedure was to allow the one electrode to serve as cathode for a given time at a given current. This is called the period of "soaking" during which the cathode absorbed gas through positive ion bombardment. The polarity of the electrodes was then reversed so that the electrode which had been soaked as cathode now became the anode. Anode spots then formed on the anode if the pressure-electrode distance conditions were suitable. The discharge was then maintained at a constant current or potential during the period of the existence of these spots on the anode.

As soon as the last spot disappeared from the anode, the discharge was stopped, since it is assumed that for a given current, the spots disappeared when the rate of evolution of the gas from the anode had decreased to a critical value. Within a few seconds after the discharge was stopped, as mentioned above, the process was repeated. Thus a series of observations which showed the effects of the soaking of the cathode on the characteristics of the anode spots were obtained.

It was observed early in this investigation that the number of spots which appeared under similar conditions of current, pressure, etc., was different depending on whether the current was increased or decreased in order to obtain the desired value. This was to be expected since the spots often formed in patterns such that a considerable change in current was necessary to change the pattern. It was necessary, therefore, to use the same applied potential difference at each closing of the switch in order to obtain consistent results in the number of spots which were formed on the anode.

Throughout the work, particular attention was paid only to the one electrode for which the gas content and previous treatment had to be known at all times.

Photographs were taken at an angle of 30 degrees with the axis of the tube. Sometimes difficulty was encountered in obtaining a satisfactorily stationary pattern. The photographs of the spots which are presented in the succeeding parts of this paper were obtained with an exposure of one-fifth second on a Voightlander camera which had an F 4.5 lens.

Results

Presentation and discussion of photographs: The photographs presented in Figure 2 were chosen because they show the relative difference in the size of the spots. In pictures *a*, *b*, *c*, and *d*, the electrodes were 41 mm in diameter, while those in pictures *e*, *f*, *g*, and *h* were 34 mm in diameter. In picture *g*, the

spots were rotating rapidly under the influence of their own magnetic field. Picture *h* which was taken perpendicular to the axis of the tube shows the hemispherical form of the spots and their appearance back of a striation.

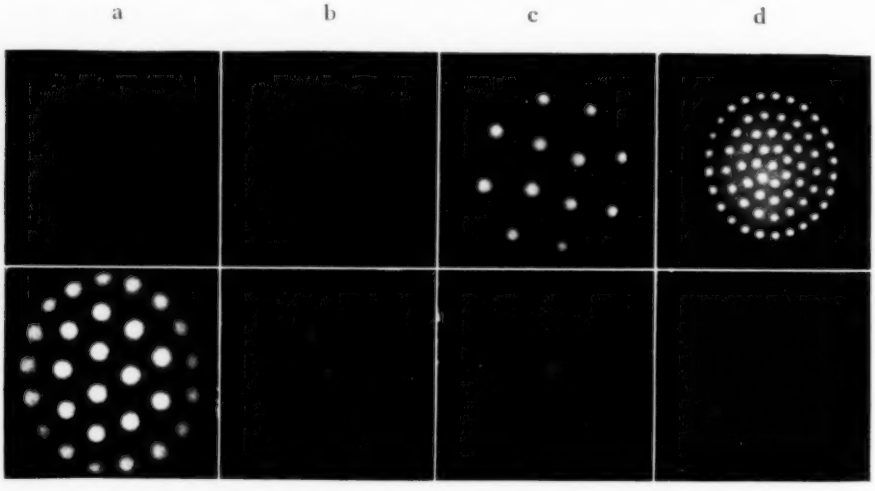

Fig. 2. Typical patterns of anode spots.

The experimental conditions for the patterns which are presented in Figure 2 are given in Table I.

TABLE I.

Pattern	Kind of gas	Gas pressure in mm Hg	Electrode separation in cm	Potential drop in volts	Current in milliamperes
a	nitrogen	0.41	10.5	825	17
b	hydrogen	2.25	16.9	880	125
c	hydrogen	5.8	12.3	625	275
d	hydrogen	3.3	14.7	881	180
e	(argon 90%) (hydrogen 10%)	9.0	10.8	690	240
f	hydrogen	3.1	13.2	920	160
g	hydrogen	3.35	14.3	1240	200
h	hydrogen	2.55	18.3	902	85

Results for different gases. Anode spots did not form in any gas when the electrodes had been sufficiently degassed provided that mercury vapor was excluded from the tube and that the discharge was set up within two minutes after the admission of the gas. In general, anode spots formed in hydrogen, nitrogen, carbon monoxide, air, and in certain gas mixtures. Spots did not form in oxygen, pure argon or pure neon. The formation of very weak spots in helium which contained a trace of hydrogen will be discussed later.

In a discharge in hydrogen, the spots formed over a gas pressure range of from 0.6 to 12 mm. The gas pressure limits varied with different gases; but in all gases, the lower pressure value was limited by the possible electrode separa-

tion and the higher pressure value was limited by the limit of the current which was available from the generator. Hydrogen was different from other gases in that, for a given pressure, the spots formed over a comparatively wide range of electrode separation which in some cases was as much as 20 cm. When striations were present in the hydrogen discharge, the spots appeared when the anode was placed in the dark space between the striations. The spots disappeared and reappeared as the anode was moved through the bright part and the dark part of the striations respectively. In case the configuration of spots was made up of several rings, the outside ring disappeared first as the anode was moved through a striation which, for the smaller electrodes, was conical in shape.

When a well-degassed electrode was allowed to remain in hydrogen for a few minutes, spots which lasted as long as a second or two were formed at the first passage of the discharge. This observation shows that the metal of the electrodes absorbed hydrogen even in the absence of an electric field. Degasification of the electrodes by means of the induction furnace after they had been used in hydrogen gas was almost as difficult as was the degasification of new electrodes.

The anode spots formed easily in nitrogen over a pressure range of 0.4 to 14 mm of mercury for available electrode separation and current limits. In nitrogen, however, the spots formed only at the beginning of the positive column within a range of two cm at most. As the anode was moved farther into the Faraday dark space, the spots gradually disappeared. When the anode was moved farther into the positive column, the configuration of spots became unstable and finally merged into the positive column. This peculiarity of limitation of the formation of spots to the neighborhood of the beginning of the positive column in nitrogen and other gases which gave a strong positive column make it impracticable to carry out as extensive investigations in these gases as in hydrogen.

Anode spots formed very readily when the anode was placed near the beginning of the positive column of a discharge in carbon monoxide. The spots which were greenish white in color in this gas, formed over a pressure range of 0.4 to 15 mm of mercury for the electrode separation and current limits of the apparatus. For a given period of "soaking" of the cathode in carbon monoxide, the spots lasted much longer than in either hydrogen or nitrogen. Moreover, degasification of electrodes, subsequent to their use in carbon monoxide discharge, was much more difficult than that of electrodes used in hydrogen or nitrogen.

No anode spots were formed in pure oxygen under any conditions. In mixtures of oxygen and carbon monoxide, spots did not form until the carbon monoxide content of the mixture had reached about 30 percent. Then anode spots which were characteristic of carbon monoxide were formed.

An electrode was "soaked" to saturation in carbon monoxide. The carbon monoxide was then removed from the tube and oxygen was substituted. Under these conditions, spots which were characteristic of carbon monoxide formed on the anode which was then full of carbon monoxide. Such spots

lasted for three or four minutes. This observation is direct proof that the anode spots are formed by gas being evolved from the anode under electron bombardment. The previous observation that 30 percent carbon monoxide in oxygen was necessary for anode spot formation precluded any possibility of the formation of these spots by any small amount of residual gas.

Anode spots were not formed in pure argon or pure neon. In these gases there was a tendency for the positive column to separate into two or more parts which rotated with respect to the axis of the tube. These streamers ended in bright spots on the anode which, however, were not of the same nature nor of the same origin as the anode spots now under investigation.

In argon, neon, and helium, the presence of mercury vapor given off from a mercury surface in the tube permitted the formation of bright anode spots. Bright anode spots also were formed when ten and five percent hydrogen was present in argon and neon respectively. Since no arrangement was made in the present apparatus for mixing and circulating the gases in the discharge tube, the above percentages may be somewhat in error. However, they are of the correct order of magnitude.

When the helium was apparently pure except for a small trace of hydrogen, very weak yellow anode spots appeared. These weak spots in helium were much larger than those for a corresponding pressure in another gas. However, these spots were symmetrically arranged and had all the characteristics of true anode spots. Bright anode spots appeared on the anode in a discharge in helium to which two tenths of one percent hydrogen had been added.

Effect of the metal of the electrodes. The effect of the metal on the formation of anode spots was studied only qualitatively. Anode spots formed on electrodes of iron, nickel, copper, aluminum, and brass. Electrodes of iron were used almost entirely for the quantitative study because its rate of sputtering was low. However, electrodes of nickel produced no noticeable change in the characteristics of the spots from those observed on iron electrodes. The thickness of the electrodes was found important only insofar as it affected the change of temperature of the electrodes.

The anode spots were not symmetrically arranged on the anode when impurities were present on the surface of the anode or when a new electrode was used as anode without previous degassing. However, the use of a new untreated electrode for a few minutes as cathode put it into such a condition that a symmetrical pattern of spots was formed when it was subsequently made anode.

The use of a barium coated electrode as cathode resulted in a decrease in the potential drop across the tube. As cathode it gave a symmetrical arrangement of spots on an uncoated electrode used as the anode; but when it was used as anode the spots were very unsymmetrically arranged, due most probably to the non-uniformity of the barium oxide layer.

Unsymmetrically arranged anode spots were formed on a carbon anode. The effects of local heating produced bright anode spots on the carbon. The carbon electrode could not be outgassed with the induction furnace. More-

over, the surface of the carbon could not be made to absorb gas uniformly by reversing the direction of the current because the discharge from the cathode was concentrated on several small areas on the carbon surface of the sleeve of this electrode. On the whole, the carbon electrode was unsatisfactory both as a cathode and as an anode. Nevertheless, anode spots were formed on its surface from the occluded gases.

Faint anode spots which were symmetrically arranged appeared on the surface of an anode of mercury in hydrogen and in the rare gases.

Rotation of the anode spots. The spots were seldom stationary on the anode for any length of time. Under the influence of the magnetic field which was set up by the passage of the current through the tube, the pattern of spots rotated with respect to the central axis of the tube, sometimes in a clockwise direction and at other times in a counter clockwise direction. The angular velocities of the spots in the various rings were not the same, the outer ring having the largest. At times the direction of rotation in two concentric rings was opposite. An increase in the distance between the electrodes increased the tendency for rotation of the pattern.

A solenoid placed coaxial with the tube, and away from the anode, so that a part of the field was radial to the electrode, could change the rotational velocity of the spots in the rings and even reverse the direction of rotation. When a solenoid was placed perpendicular to the axis of the tube in the immediate region of the anode, the configuration of spots was deformed by the magnetic forces so that the spots then appeared in a deformed circular pattern which also rotated rapidly during the application of the magnetic field of the solenoid. An unstable and unsymmetrical pattern of spots always formed when the walls of the tube in the neighborhood of the anode were badly sputtered.

Size and shape of electrodes. Circular electrodes of 41 mm and 34 mm in diameter were used. Under the same experimental conditions, the size of the spots was larger on the larger electrodes.

The use of a small spiral incandescent tungsten cathode did not destroy the symmetry of the anode pattern of spots when this cathode was placed on the line of the axis of the anode.

That the pattern of spots was governed primarily by the shape of the anode was proved by the use of a circular cathode and a triangular anode on which the spots formed in a triangular pattern which contained as many as four distinct triangles with their sides parallel to the edges of the anode. When the electrodes were placed so close that the form of the cathode influenced the field at the anode the spots on the anode were equally spaced on the sides of the triangles, but when the electrode separation was increased to some extent, the spots, except those forming the vertices of the triangles, tended to concentrate toward the middle of the sides of the triangles, but even then the form of the triangle was not destroyed.

When the electrodes were not parallel, an asymmetrical arrangement of spots always resulted. Under these conditions, the angular velocity of a spot was not uniform. Its angular velocity was greatest where the separation of the electrodes was greatest.

When the electrodes were parallel their centers were not on the same horizontal lines. The pattern of spots was displaced from one edge of the anode.

Size and intensity of anode spots. In general the size of the spots increased with an increase in the gas content and temperature of the electrode, with a decrease in the gas pressure, with an increase in the size of the electrode, and slightly with a decrease of the distance between the electrodes. The size of the spots definitely decreased with an increase in current and voltage. It also decreased with an increase in the age of the spots, although, for constant potential, the current decreased during their life.

Figure 3 is composed of two photographs of patterns of anode spots in hydrogen at 2.6 mm pressure and electrode separation of 17.2 cm. The pattern on the left was formed by 210 milliamperes at 1300 volts and the pattern

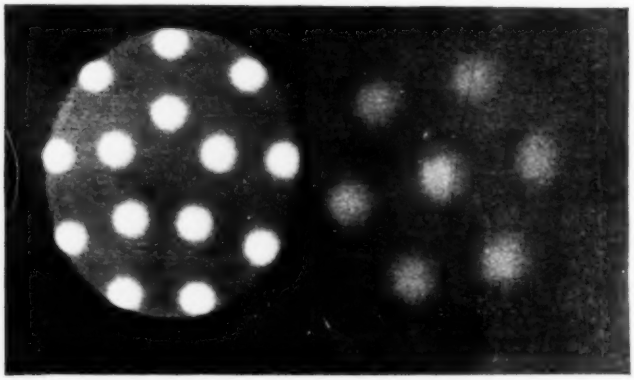

Fig. 3. Change of number of spots with change in current and voltage.

on the right by 30 milliamperes and 725 volts. These photographs show the change in the number and in the intensity of the spots with a change of current and voltage.

The change of the size of the spots with the change of temperature of the anode is shown in Figure 4. These photographs were taken as a discharge

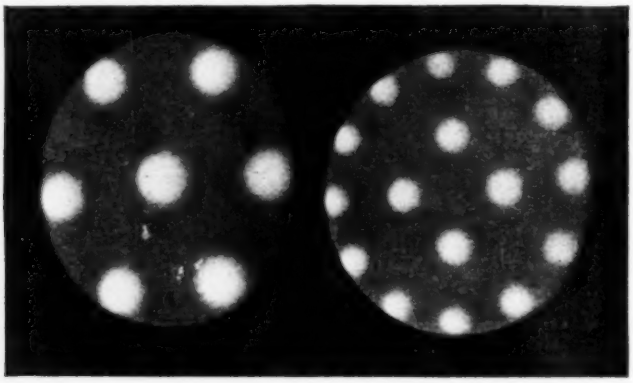

Fig. 4. Change in size and number of spots with change in temperature of anode.

passed through hydrogen at a pressure of 2.45 mm between electrodes separated 17.7 cm. The picture on the right is that of an anode which was saturated with gas by means of soaking it previously as cathode. This picture was taken after the electrode had cooled to room temperature, with a current of 115 milliamperes at 1120 volts. The picture on the left was taken while the anode was still red hot from its previous use as cathode, with a current of 115 milliamperes and 1100 volts.

The intensity of the spots increased with an increase in current and voltage. To a small degree, it depended on the kind of gas. Hydrogen gave brighter spots than nitrogen. The intensity was quite high when a rare gas was mixed with hydrogen or mercury vapor.

Factors which influence the number of spots. The number of spots which appeared in the pattern on the anode increased with an increase of pressure, with an increase in current, with an increase in the amount of gas in the surface of the anode up to a saturation value, and slightly with an increase of distance between the electrodes. An example of the increase in the number of spots with an increase in current and voltage is given in Figure 3 above. The number of spots decreased with an increase of the temperature of the anode within certain limits. An example is given in Figure 4.

The same pattern of spots was obtained after a thirty second period of soaking of the electrode as when the electrode was soaked ten minutes provided that the temperature change in the electrode during this latter period was not over two hundred degrees. This indicates that the condition of the surface layer or near surface layer governed the number of spots and that this layer quickly reached saturation.

Mention has already been made of the observation that spots were formed from gas which was absorbed by mere contact with the metal. The following experiment showed that spots were also formed by gas which diffused to the surface of the anode. The cathode was soaked with hydrogen gas until saturation was reached, then it was used as anode until the spots disappeared. Immediately afterward the tube was evacuated to a pressure less than 2×10^{-4} mm at which pressure it remained for forty-eight hours. At the end of this period, hydrogen was again passed into the tube until a pressure of 3.3 mm was reached. Forty spots in four rings were present when the discharge was established within a few seconds after the gas was admitted. At the end of 25 seconds the number of spots had decreased to 30 in three rings. The remainder of the spots disappeared simultaneously at 30 seconds.

The large number of spots which appeared under the above conditions and the short life of the spots indicate that the gas, which had penetrated to a considerable depth in the electrode diffused to the surface or to the layers immediately underneath the surface. Since a considerable amount of gas was given off from the anode only during a thirty second period, one may conclude that the gas which diffused to the surface, was held there

by the molecular forces of the metal. Since no similar effect was observed when a degassed electrode was treated in a similar manner, it is not probable that these spots were formed from hydrogen absorbed while the electrodes were subjected to the low gas pressure given above.

Application of the phenomenon of anode spots to the study of the rates of absorption and emission of gases by the electrodes of a Geissler discharge: Let us assume that the cathode of a direct current Geissler discharge absorbs gas under the influence of positive ion bombardment at a rate which is a function of the number and energy of the positive ions which strike and of the gas content of the cathode at that particular moment. Let us further assume that the anode emits its absorbed gas under the influence of electron bombardment at a rate which is a function of the velocity of the electrons at the moment of striking, of the number striking, of the gas content of the anode, and of the kind of gas.

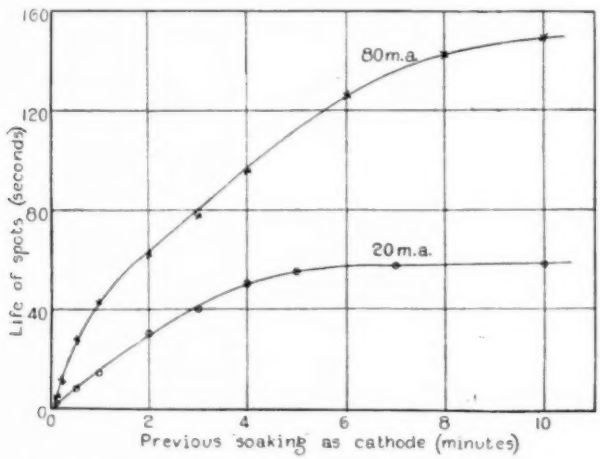

Fig. 5. Life-soaking curves for different soaking currents.

In order to test the validity of the above assumptions a series of experiments was carried out in hydrogen. Typical results are given in Fig. 5. The lower curve was obtained by subjecting the cathode to soaking in 3mm of hydrogen with a current of 20 milliamperes for different periods. At the end of each of these periods of soaking, the direction of the discharge was reversed and a current of 110 milliamperes was passed through the discharge until the last spot had disappeared from the anode. The lower curve of Figure 5 shows that, with a soaking current of 20 milliamperes, the life of the spots approached a constant value with a soaking period of 5 minutes. However, when a soaking current of 80 milliamperes was used the life of the spots was relatively longer as shown in the upper curve.

We believe that the differences in the lives of the spots for different soaking currents were due to differences in the rates of the absorption and in the total amount of gas absorbed. This difference in absorption was due to the difference in the temperature of the cathode during positive ion bombardment

and to the difference in the energy of the impinging positive ions under the two conditions.

Many similar curves were obtained in hydrogen with both the small and the large experimental tubes. The rates of absorption and emission of hydrogen changed with the change of conditions in the electrode. However, for a series of runs on the same day, the same type of curves was obtained. It was not possible to retrace the curves backwards because of a change in the temperature of the electrode in the long periods of soaking. For soaking currents between 20 and 80 milliamperes the curves fell between those given in Figure 5.

Since the charge on the walls of the tube influences the electric field at the anode and since the ratio of the random current to the drift current in the tube governs the anode drop, it was deemed advisable to investigate the effect of the diameter of the tube on the anode spots. To this end a tube of 10 cm was substituted for the tube of 6 cm diameter. The use of the larger tube resulted in a greater stability and uniformity of the pattern of the spots, less rotation of the spots and a longer period of use before cleaning was necessary. However, no appreciable difference appeared in the life-soaking curves which were obtained from the different tubes when the walls of the tubes were equally free from sputtered material. It was to be expected that a greater electrode separation would be required for the larger tube, because the length of the negative glow increase with an increase in the diameter of the tube.

It was possible to obtain curves as those given in Figure 5 only in hydrogen because in all gases having a strong positive column the change in the potential drop across the tube with the change in the gas content of the electrodes altered the position of the beginning of the positive column to such an extent that the anode was soon out of the narrow region in which the formation of anode spots was possible. However, in the case of carbon monoxide gas, the anode was moved through a small distance in order to keep it in the region of the anode spots. This method showed that the life of the spots for carbon monoxide, for a given amount of soaking, was considerably longer than that of hydrogen for similar soaking. This observation is only qualitative because the potential drop across the tube changed with the change in the distance of electrode separation.

Figure 6 contains the life-soaking curves for the same electrodes under the same conditions except that the curves were taken on consecutive days in the order given in the figure. Curve I, was obtained with new electrodes which had been carefully degassed by heating in vacuo by means of the induction furnace. Between the time of obtaining curves I and II, a discharge was maintained in the tube for short periods which totaled four hours after which the electrodes were again degassed by heating in vacuo. A similar procedure took place between the time of taking the data given in the consecutive curves of Figure 6. These curves show that the life of the spots increased with the use of and the degassing of the electrodes. On the assumption that a certain rate of evolution of gas from the anode is neces-

sary for the formation of anode spots, these curves show that the anode evolves gas for a longer time above that rate when the electrode is used in a discharge and is subsequently degassed.

In order than an electrode, under constant current conditions, evolve gas above a certain rate for a longer period, it must contain a greater amount of

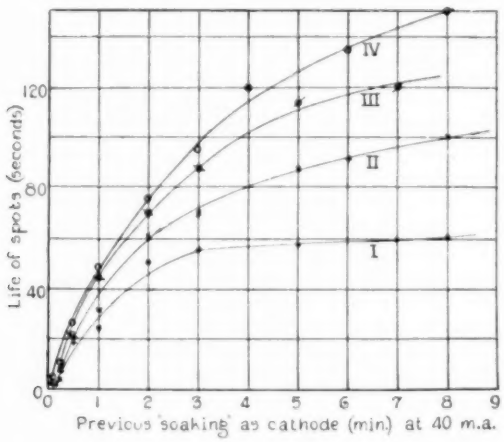

Fig. 6. Life-soaking curves showing effect of aging of electrode.

gas to begin with or the rate of evolution of gas must be more gradual or both conditions must be fulfilled. For this we give the following explanation.

It is certain that some of the gas ions which are driven into the anode structure by considerable electrical force are more difficult to remove than are the molecules of the original occluded gas. Hence, degassing by means of heating

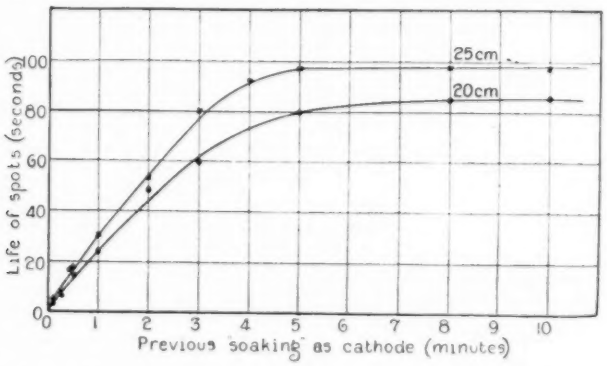

Fig. 7. Life-soaking curves for different electrode separations.

in vacuo may not be so efficient in removing such gas molecules. Therefore, the electrode may contain more gas to begin with even after the same period of degassing than it did before it was used so much as cathode. On the other hand, the spacing of the molecules of the metal may be so changed by use and subsequent degassing, that the hydrogen molecules will then be absorbed more readily as they strike the cathode in the form of positive ions. Also they may penetrate deeper into the metal of the cathode.

Experimental evidence, which supports this hypothesis, is given by Yamada[5] who found that absorption of hydrogen in palladium resulted in a uniform expansion in the space lattices and by Baum[6] who found that hydrogen ions under the influence of 3000 volts not only penetrated a silver cathode to some distance but that they also produced fissures in the crystal structure of the metallic electrode.

The life soaking curves which are presented in Figure 7 were obtained from data in which the experimental conditions except the change in electrode separation were kept constant, as nearly as possible. These curves show that the life of the spots increases with an increase in the electrode separation. This increase of the life of the spots with increase of electrode separation was not due to temperature increase or aging effect of electrodes because the data for the curve at 20 cm were obtained immediately after that used in the curve at 25 cm.

Since the electrode contained approximately the same amount of gas in both cases at the end of similar periods of soaking, and since the number of electrons striking the anode was also the same, this difference in the life of the spots for different electrode separations must have been due primarily to a difference in the velocity of the electrons at impact on the anode by which the rate of evolution of gas would have been different.

This change in the velocity of impinging electrons could have been produced by a difference in the electric field depending on the position of the anode especially if it was placed near the beginning of the positive column. Moreover, a change in the anode drop of potential may produce a greater change in the energy of impact of an electron on the anode than that which corresponds to a change of V in the relation $eV = 1/2\ mv^2$. For instance, if the anode drop of potential is just greater than the ionizing potential of the gas, some of the electrons will make ionizing collisions with the gas molecules in the region of anode space charge, and will thus lose most of their energy. Such electrons will then strike the anode with much less energy than that of the electrons which make only elastic collisions with molecules because their velocities are below that which corresponds to the velocities necessary for ionization or excitation of the gas molecule.

Change of potential with the change in the gas content of the electrode. In Figure 8 are given the time-voltage curves during the life of the anode spots for a constant current of 110 milliamperes in hydrogen at 3 mm pressure and electrode separation of 22 cm. The anode in the discharge from which the data for these curves were taken was soaked at 40 milliamperes for the different periods given in this figure. These curves show that the anode spots disappeared in each case at approximately the same voltage. When the experiment was continued beyond the time of the disappearance of the spots the potential drop approached a constant value of which there is some evidence in these curves. (The curves in the Figure 9 show this more plainly.) We belive that the constant potential drop was determined by the conditions in the tube reaching a state of equilibrium, that is, the change in the gas content of the electrodes must have reached a steady state. These curves

also show that, at least within given limits, the potential drop, immediately after the initiation of the discharge was lowered by an increase in the soaking period of the cathode. Each of these curves corresponds to the determination of one point of the life-soaking curve such as given in Figure 6.

The differences in the potential drop for the discharge as shown in these curves were due almost entirely to different amounts of gas in the electrodes. Different amounts of gas were obtained in each electrode by varying the time of reversal of the current during which the cathode absorbed gas and the anode emitted gas. Degassing the cathode by means of an induction furnace resulted in a lower maintaining potential at the beginning than that given in curve VI of Figure 8.

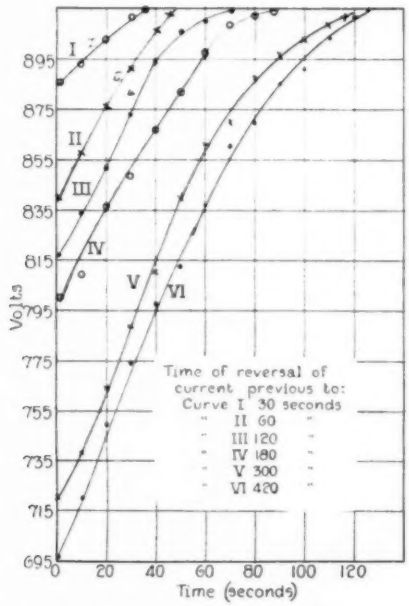

Fig. 8. Time-voltage curves during life of spots.

That the differences in the maintaining potential which are evident in the several curves and in each single curve at different times, were due almost wholly to the processes at the cathode was proved by the following experiment. Two new iron electrodes *A* and *B* were degassed in vacuo by an induction furnace to an equal degree. Then electrode *A* was made cathode and electrode *B* anode in a discharge of 100 milliamperes in hydrogen at 2.8 mm pressure. The variation of the voltage with time is given in curve I, Figure 9.

Since both electrodes were degassed to begin with most of the change in potential difference was due to absorption of gas at the cathode since electron bombardment could free few gas molecules from the already degassed anode.

Upon reversal of the direction of the discharge at the end of three minutes, results were almost identical with those given in curve I although in this case

the cathode was a degassed electrode but the anode contained gas as a result of previous use as cathode for three minutes. Thus we found that degassed cathode and anode produced the same time voltage characteristics as a degassed cathode and a gas filled anode. From this we conclude that the evolution of gas from an anode under electron bombardment has little or no effect on the potential drop of the discharge.

Subsequently, electrode *A* which contained some gas was made cathode and the results given in curve II of Figure 9 were obtained. The main difference in the curves I and II is a higher starting potential difference when the cathode contained some gas. The irregularity of curve I between 60 and 100 seconds is typical of the curves obtained with new electrodes which were degassed by the induction furnace. We believe the change in potential to

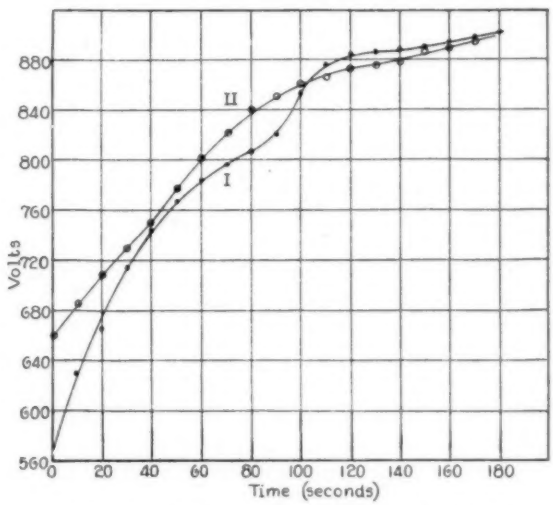

Fig. 9. Time-voltage curves with new electrodes.

be due to evaporation of impurities from the surface of the cathode, impurities which were brought to the surface of the metal during the first heat treatment.

Discussion of Results

Summing up the behavior of the anode spots, we see that their formation and existence must depend on the joint action between the gases released from the anode and the electron stream to the anode. From their magnetic behavior and from their dependence on the distance between the electrodes, we deduce that they must be the manifestations of a splitting up of the electronic current into discrete and more or less stable "rays" or current-beams. Also, since their life was, within limits, proportional to the length of time the electrode had previously been used as cathode, since their number decreased with the time that the electrode was used as anode, since no spots formed on a well outgassed anode, and since spots having the color characteristic of carbon monoxide formed in a discharge in oxygen on an anode previously

soaked in carbon nomoxide, we infer that gas must escape from the anode in order that the formation of electron beams and their resultant anode spots be possible.

On the assumption that one necessary condition for the formation of anode spots is the evolution of a certain amount of gas from the surface of the anode when it is subjected to electron bombardment, we shall now give an explanation of the formation of the anode spots.

When no gas is liberated by the anode, the electrons form a space charge sheath which limits the more intense part of the field to within a short distance of the anode,[9] of the order of a few millimeters at the pressure used. Outside the sheath the electric intensity is so small that the drift velocity of the electrons due to the field is not sufficient to keep them in relatively straight paths parallel to the axis of the tube, and they scatter by successive collisions with the gas molecules until the slowly drifting stream fills the cross section of the tube.

When these electrons enter the sheath, their increased speed causes them to fall to the anode in nearly straight lines. It is, then, in this sheath, where the field is large, that there is any possibility of formation of electron beams; and the chance of their formation increases as the sheath increases in thickness.

If, now, gas is emitted from the anode, the molecules will either already be ions, or will soon become ions by collision with electrons, and these ions will partially neutralize the electronic space charge, thus increasing the sheath thickness and decreasing slightly the anode fall of potential, and therefore making the formation of beams more probable. Inasmuch as one positive hydrogen molecular ion neutralizes the space charge of three hundred or more electrons a small quantity of gas from the anode will cause a large change in sheath thickness, and under these conditions the electrons will move in straight paths for a centimeter or more before striking the anode.

Only a small portion of the current will be concentrated in the spots, for the gas will scatter many electrons to the other parts of the anode. These rays will be the favored paths, however, and the fastest electrons, those which have suffered few collisions, will travel therein. These faster electrons will create more ions than the other scattered ones, and so, a short time after the discharge is started, these beams will act as separate phenomena superimposed on the back-ground of scattered electrons, having their own potential distribution, their own motions, and their constant current density. This current is probably due predominantly to the ions created by the original electron beam in the gas coming from the anode. For this reason, and because the gas from the anode increases the sheath thickness, it is probable that the number of spots or beams present is proportional to the amount of gas evolved by the anode.

Since anode spots form only at the beginning of the positive column in gases which have a strong positive column and since they form before the first striation and in each dark space between successive striations when

[9] Langmuir, Gen. Elec. Rev. **27**, 767 (1924).

striations occur in the tube, it is now necessary to show why the spots form on the anode when it is placed in these positions.

Langmuir[9] explains how an electron sheath around an anode may be broken down suddenly, through its neutralization by positive ions which are formed in the space charge sheath, to such an extent that the anode drop falls discontinuously to a lower value. He found that, when breakdown occurred, the anode glow usually appeared in the form of a sharply defined hemispherical region several times more luminous than the surrounding region. In this explanation, he assumes that very few gas molecules are present in the electron space charge sheath so that only a small fraction of the electrons which pass through this sheath make ionizing collisions. He further assumes that the gas molecules which are present in this sheath come into the sheath from the region on the outside of the anode sheath.

However, it is apparent from his theory that the breakdown of the electron sheath will be brought about the more easily the greater the concentration of gas molecules in the space charge sheath since a larger percentage of the electrons then make ionizing collisions with the gas molecules in their passage through the space charge sheath. Thus we see that the emission of gas from the anode will assist in the neutralization of the space charge sheath, which results in an increase in its thickness and a decrease in the total anode drop of potential.

It is evident from the preceding discussion that the electron space charge sheath will increase in thickness or breakdown (in the sense as used by Langmuir) more easily in the regions where the field is small. Therefore, the anode spots, whose appearance is due to the increase in the thickness of the electron space charge sheath of the anode or to its breakdown, will form when the anode is placed in the region at the beginning of the positive column where the electric field has not yet attained the maximum value of the positive column. In the dark space regions between striations, the field is again small. Therefore, these dark space regions between striations will also be favored regions for the formation of anode spots.

A field which is below that necessary for the production of an anode glow by ionization is excluded from this consideration. Consequently, the region of the Faraday dark space is excluded because there the anode drop of potential is too low to produce ionization, so that one would not expect the formation of anode spots.

We believe that anode spots do not form in oxygen because the oxygen ions, on striking the cathode, react with the metal of the cathode to form stable compounds which are not decomposed under subsequent electron bombardment of the anode.

Since the rare gases, helium, neon, and argon do not react chemically with any substance under any condition, and since very little gas was evolved in the degasification of electrodes subsequent to their use in these rare gases, we infer that these gases are not absorbed by the metal of the electrodes in amounts which are capable of producing anode spots. We believe that very weak yellow anode spots were formed in helium which contained a trace of

hydrogen whose presence could be detected by means of a direct vision spectroscope because the anode space charge sheath was not sufficiently broken down by the presence of a few hydrogen ions to permit the formation of bright spots.

Considering the effects of absorption of hydrogen by an electrode in a mixture with the rare gases and the production of hydrogen ions by collision with excited atoms, we have been able to explain, to our own satisfaction, the formation of bright anode spots when 10 percent, 5 percent and two tenths of one percent of hydrogen is present in argon, neon and helium, respectively.

When mercury is present in the discharge tube, sufficient mercury molecules are present on the surface of the anode to bring about the formation of anode spots in each of the rare gases. Anode spots appeared under similar conditions of the gas as those described by MacKay[8] who photographed the spots in a discharge in helium containing mercury vapor. MacKay reports in the same paper the formation of spots of similar nature when mercury was excluded from the discharge tube. In that event, the helium which he used must have had, as impurity, hydrogen to the extent about two tenths of one percent. From the nature of the spots formed when a trace of hydrogen was present in the helium, it is doubtful if anode spots will be formed at all in pure helium.

Since anodes spots are formed by beams of electrons we would expect these beams to be influenced or even rotated by the application of a suitable external magnetic field. We offer the following explanation for their rotation in the absence of a magnetic field.

The drift current approaches the anode in the form of a frustrum of a cone rather than in the form of a cylinder so that there will be present in the tube a small resultant radial magnetic field which will be sufficient under certain conditions to set the whole pattern in rotation. As the electrodes are separated farther apart, the influence of the electrodes on the drift current will be less, so that some of the drift current will approach the anode at a greater angle with the axis of the tube in a manner which may be likened to the change of the lines of electric force. Then the radial component of the magnetic field will be greater so that the angular velocity of the pattern will be increased.

In order to explain the change of sense of rotation of the pattern, the rotation in the opposite sense in consecutive rings and even the formation of a stable pattern, one would have to consider, in addition to the component of the magnetic field already discussed, the magnetic field set up by the diffusion of the electrons to the walls.

Since a given rate of emission of gases from the anode is necessary for the formation of anode spots, this phenomenon can be used as a measure of the rate of emission of gas from the anode and indirectly as a measure of gas absorption by the cathode. By the application of this method, we find that a cathode absorbs certain gases in proportion to the time of soaking up to a certain saturation value which is determined by the current and voltage of soaking, the temperature of the cathode and the previous treatment of the

electrode. We also find that the anode emits both absorbed and original occluded gas when it is subjected to electron bombardment.

Finally, in consideration of the evidence which follows, we believe that the absorption of hydrogen gas by the cathode of a Geissler discharge increases the potential drop across the tube until saturation of the cathode with gas is reached.

1. The potential drop increased with time until it reached approximately a constant value which depended upon the current density and the temperature of the cathode, in almost the same way that the life of the anode spots increased with an increase in the period of soaking of the cathode for a similar current density.

2. Degassing an electrode previous to its use as cathode either by having it serve as anode in a Geissler discharge or by heating it in vacuo with induction currents resulted in a decrease in the potential necessary to maintain the discharge for a short time after the discharge had struck. This decrease was a function of the amount of gas which had been emitted from the electrode in degassing.

3. After a discharge had been discontinued for a time, the potential drop was always lower at the second initiation of the discharge than it was just previous to the time of its discontinuation.

4. Although the cathode contained different amounts of gas to begin with in different experiments under the same conditions, the potential drop approached the same limit in each case as the cathode approached saturation in absorption of gas.

5. Experiments under identical conditions, except that in one case the anode was full of gas and in the other it was thoroughly degassed, gave almost identical time voltage curves. This we take to be good evidence that the emission of gas from the anode has little or no effect on the potential drop of a discharge.

We wish to express out indebtedness to L. B. Headrick and Dr. P. M. Morse for helpful suggestions in this work.

ELECTRON VELOCITIES IN A HIGH FREQUENCY DISCHARGE IN HYDROGEN

By Charles J. Brasefield
University of Michigan

(Received November 20, 1929)

Abstract

A high frequency discharge in hydrogen was obtained by applying undamped high frequency voltages to the movable external electrodes of a cylindrical discharge tube. The mean velocity of the electrons in the discharge was determined from the ratio of the densities of certain singlet and triplet lines of the molecular spectrum of hydrogen. It was found (1) that the electron velocity increases as the voltage between electrodes is increased, the gas pressure and the frequency of oscillation being constant; (2) for a given voltage between electrodes, the electron velocity is, in general, greater the longer the wave-length of oscillation; (3) the electron velocity decreases as the pressure is increased. The paper concludes with a discussion of the mechanism of the high frequency discharge in which an explanation of its behavior is proposed.

Introduction

IN THE study of any sort of gaseous discharge, one of the more important items of interest is the mean velocity of the electrons in the discharge and its variation under different conditions. The high frequency discharge with external electrodes is a very peculiar type of gaseous discharge. Studies have been made of numerous characteristics of this discharge, such as the striking and maintaining potentials[1] and the conductivity[2] but to the writer's knowledge no one has succeeded in determining the mean electronic velocity in the discharge. As a matter of fact, it would appear to be extremely difficult, if not impossible, to make such measurements by the ordinary method applied in arcs and glow discharges, namely, the Langmuir exploring electrode method. It has been suggested[3] that the mean electron velocity in a high frequency discharge in hydrogen might be determined from the ratio of the densities of certain singlet and triplet lines of the molecular spectrum of hydrogen. This method has been employed with more or less success in the present work.

Apparatus

To produce the high frequency oscillations, two U. X. 852 75-watt tubes were used in push pull in an ordinary Colpitts circuit, which is shown diagrammatically in Fig. 1. The plate voltage was supplied by a 2 KW, 3000 volt transformer, T_1, and measured by an electrostatic voltmeter, V.

[1] R. L. Hayman, Phil. Mag. **7**, 586 (1929) and others.
[2] H. Steinhauser, Zeits. f. Physik **54**, 788 (1929).
[3] C. J. Brasefield, Phys. Rev. **34**, 437 (1929).

One quarter ampere fuses, *F*, protected the plates from overloading. The radio frequency chokes, *R.F.C.*, were made of #30 B. & S. copper wire, *S.C.E.*, wrapped on 3-inch bakelite tubing; 65 turns for 15, 25, and 50 meters, 180 turns for 100 meters, and 300 turns for 200 meters. The mica condensers C_1 had a capacity of 0.002 μf. and could stand 2500 volts. The variable air condensers C_2 had a capacity of 0.00045 μf. and were carefully calibrated. The inductance L was a coil of 3/16 inch copper tubing 3.5 inches in diameter; 2 turns for 15 meters, 3 turns for 25 meters, 5 turns for 50 meters, 10 turns for 100 meters, and 30 turns for 200 meters. The electrodes surrounding the discharge tube were of sheet copper 2 cm wide. Copper ribbon 1/4 inch wide was used for wiring the tank circuit and the tank current was measured by a 0-15 ampere radio frequency ammeter *A* (thermocouple type). The grid leak, *G.L.*, was a 40,000 ohm wire wound resistor to dissipate about 100 watts. The filament current was supplied by a 175 watt, 12 volt transformer T_2, across whose secondary were the by-pass condensers $C_3(0.002\mu f)$.

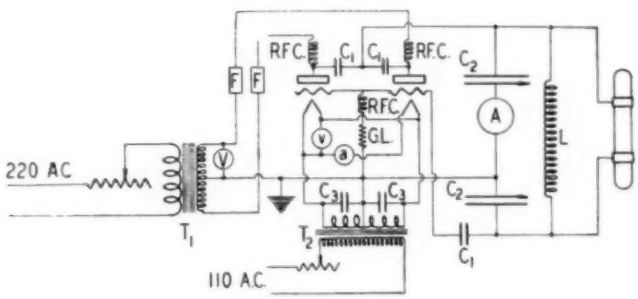

Fig. 1. Diagram of oscillatory circuit.

The discharge tube was of Pyrex glass, 30 cm long and 4.5 cm in diameter, with an optical glass window sealed into one end. Hydrogen was admitted to one end of the tube by means of a platinum tube and was pumped out at the other end, thus insuring a continuous flow of pure hydrogen. The platinum tube was 20 cm long, 1 mm in diameter with 0.1 mm walls. It was surrounded by a glass jacket through which commercial hydrogen was flowed. On heating the platinum tube to a dull red heat (about 600°K) by passing a current of about 16 amperes through it, an adequate flow of hydrogen was obtained through the discharge tube. The pressure could be varied either by changing the temperature of the platinum tube or by means of a valve which regulated the rate of pumping. Pressures were measured by a McLeod gauge.

Procedure

The voltage between electrodes, which is equal to the voltage across the condensers C_2 was calculated from the formula $E=I/2\pi fC$ where E is the voltage across the condensers, I is the current through them in amperes, f is the frequency of oscillation and C is the capacity in farads of the two

condensers in series. The condensers C_2 were always adjusted so as to be of equal capacity. Hence, the ammeter A was at a potential node and its readings were independent of its capacity to earth.

A series of runs was taken at frequencies of oscillation corresponding to 15, 25, 50, 100, and 200 meters wave-length. The pressure was kept constant at 0.03 mm and the distance between electrodes was 5 cm. For each run, the tank current I, and consequently the voltage between electrodes E, was varied between the widest limits possible. The minimum voltage was

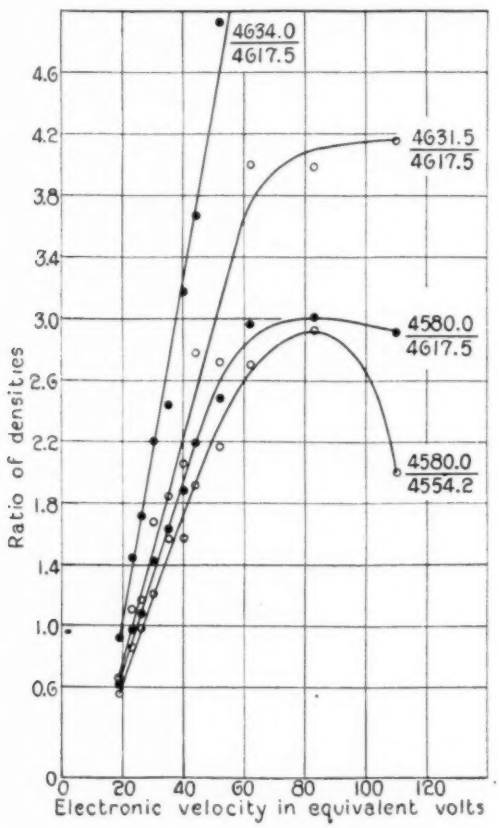

Fig. 2. Variation in the ratio of the densities of singlet and triplet lines with the electronic velocity (taken from Phys. Rev. **34**, 437 (1929).

approximately that at which the discharge first struck. The maximum voltage was determined by the output of the oscillator, that is, the voltage at which the plates of the valves became red hot.

Between these limits, photographs were taken of the discharge at regular intervals. The spectrograph used was a fairly fast two-prism glass instrument. Exposures were taken on Cramer Hi-Speed plates and were all of five minutes duration. Microphotometric traces were then made of all the spectra by means of a Moll self-registering microphotometer. From these traces, the density of the singlet line 4631.5 and the triplet line 4617.5 were

obtained by use of the relation: density = log $d/d\text{-}h$, where d is the total galvanometer deflection in the absence of a line and h is the height of the peak on the trace corresponding to the line.

From the ratio of the densities of these two lines, the electron velocity could easily be determined since the variation in this ratio with electron velocity is already known[3] (see Fig. 2). It might be remarked that although the curves of Fig. 2 were obtained using electrons of uniform velocity, they also can be used to find the *mean* electronic velocity; for the contribution to the ratio of the densities of 4631.5 to 4617.5 of those electrons whose velocity is greater than the mean will be balanced by the contribution of the elec-

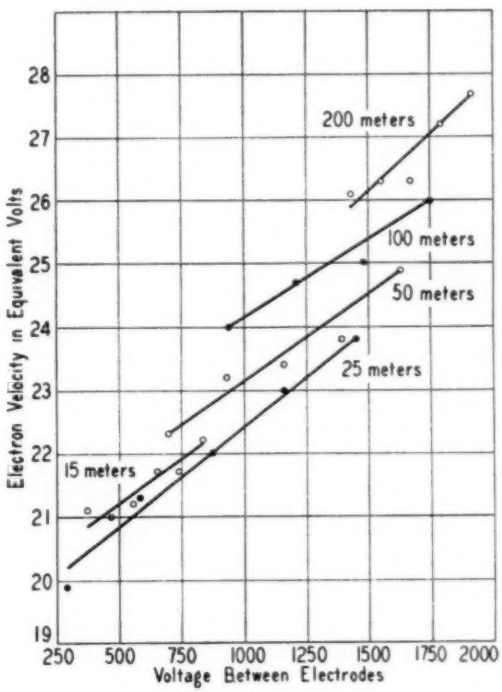

Fig. 3. Variation in electron velocity with voltage between electrodes and frequency of oscillation.

trons whose velocity is less than the mean—provided always, that the mean velocity lies on the straight part of the curves.

Results

Variation of electron velocity with voltage and frequency. The variation in electron velocity with voltage between electrodes and frequency of oscillation is shown in Fig. 3. At all wave-lengths, the electron velocity increases as the voltage between electrodes is increased. Moreover, for a given voltage between electrodes, the electron velocity, in general, increases with the wave-length of the oscillation. (The electron velocities at 15 meters seem to be an exception to this). The error in this method of finding electron velocities

is estimated at 2 volts while the experimental error is something under 0.5 volts. In other words, if two electron velocities were found to be 20 and 24 volts, they both might be in error by 2 volts, but their difference would not be in error by more than 0.5 volts.

Variation of electron velocity with gas pressure. To find the variation of electron velocity with gas pressure, a series of exposures were taken at various pressures between 0.01 mm and 0.06 mm. The wave-length of the oscillations was 25 meters, distance between electrodes 7 cm and voltage between electrodes 1020 volts. Since the ratio of the densities of the singlet and triplet lines varies with pressure as well as with electron velocity, it was necessary to correct the values of the ratio of 4631.5 to 4617.5 for the change in pressure. To the writer's knowledge, there has been only one attempt to find the effect of pressure on the excitation of the secondary spectrum. The results presented in that paper[4] were of such a nature that the correcting factor could only be calculated roughly. Very approximately, then, it was found that the mean electron velocity decreased from 25 volts at 0.01 mm to 23 volts at 0.06 mm. pressure.

Variation of electron velocity with distance between electrodes. In general, a change in the distance between electrodes produced only a slight change in the electron velocity. At 15, 50, and 100 meters, increasing the distance between electrodes seemed to produce a slight increase in electron velocity, while at 25 and 200 meters, a slight decrease in electron velocity was found.

Discussion

It is not difficult to understand why the mean electron velocity should increase when the voltage between electrodes is increased, and decrease when the pressure is increased; but at first one does not see why the electron velocity should increase when the wave-length of the oscillations is increased. To understand this, it will be necessary to consider more in detail the functioning of a high frequency discharge with external electrodes.

In a direct current Geissler tube discharge, with cold cathode, we know that the discharge is started by a few stray electrons in the gas which, under the action of the electric force between electrodes, produce more electrons by ionizing gas molecules. In this way, the number of electrons is increased to the point where the discharge strikes. Because of the unidirectional current, it is essential that there be a source of electrons, namely, the cathode. This source of electrons would not have been necessary, however, if the direction of the applied electric force were reversed before the electron cloud had time to disperse (by leakage along the walls of the tube, recombination with positive ions, etc.). This condition of affairs is obtained by applying high frequency electric forces to the discharge and since a source of electrons is no longer necessary we are able to use external electrodes.

Before a high frequency discharge will strike, however, a second condition must be fulfilled, namely, that the electrons shall attain ionizing velocity before they reach the end of the discharge tube. As a matter of fact, they

[4] P. Lowe, Trans. Roy. Soc. Can. **20,** 217 (1926).

probably must attain ionizing velocity before they have travelled the distance between the electrodes, since it is in this interval that they are under the influence of the electric forces. If, now we keep the voltage applied to the electrodes constant and increase the wave-length of the oscillations, it is evident that the time required for the electric force to reach its maximum value becomes longer and longer. Consequently, it will take the electron more time to reach ionizing velocity at the longer wave-lengths than it does at shorter wave-lengths. In other words, if an electron is to reach ionizing velocity in the same time at two different wave-lengths, the applied voltage must be increased for the longer wave-length, which means that the minimum striking potential will increase with the wave-length of the oscillation. This fact has been verified in the present experiments (see Fig. 3) as well as in those of others.[1]

It has also been shown by others[2] that a discharge has its maximum conductivity under the same conditions that give the minimum striking potentials. Hence, by referring to Fig. 3, we must conclude that the conductivity of the discharge decreased with increasing wave-length. So if the discharge were operated at two different wave-lengths of oscillation, but with the same voltage applied to the electrodes, we would expect to find a smaller drop in potential along the positive column of the discharge which had the greatest conductivity. That is, for equal voltages applied to the electrodes, there will be a smaller drop in potential along the positive column of the discharge when it is operated at shorter wave-lengths. Consequently, at shorter wave-lengths, we would expect to find smaller electron velocities. This explains why, for a given voltage applied to the electrodes, the electron velocity increases with the wave-length of the oscillations.

The writer wishes to express his appreciation to the Grigsby-Grunow Company of Chicago, Illinois, which has supported this investigation. He is also indebted to several members of the Department of Physics for their interest in this work and especially to Mr. J. S. Owens, who assisted in the experimental work.

SECONDARY ELECTRONS OF HIGH VELOCITY FROM METALS BOMBARDED WITH CATHODE RAYS

By Paul Berthold Wagner
Stanford University

(Received November 20, 1929)

Abstract

The magnetic spectra of high-speed secondary electrons emitted by Au, Ag, and Al, when bombarded with cathode rays of from 16 to 40 kv., have been photographed and densitometered. Beginning at the high-velocity end, the density is zero down to energy eV_0, equal to that of a primary ray, then rises rapidly to a maximum at about $0.94eV_0$ for Au or Ag, or $0.85eV_0$ for Al, and then declines. The density is everywhere continuous. Its first derivative may be discontinuous at eV_0, but nowhere else.

Thin targets show spectra sufficiently like those of thick targets to indicate that most of the secondary electrons come from very near the surface: for Au, within 0.2 micron even up to 40 kv; for Ag, over 0.2 micron only above 20 kv; for Al, over 0.5 micron only above 20 kv.

Obituary Notice

It is with great regret that we must record the death of the brilliant and promising young scientist whose work is described here. With his great enthusiasm for research, his conscientious thoroughness both instinctive and cultivated by his early education in Germany, and his unusually likable personality, he had every prospect of success and enjoyment in scientific research, and his death was a great loss, both to science and to his friends.

This paper is taken from his thesis for the degree of Master of Arts. As his death occurred in the sinking of the *San Juan*, on his way home to Los Angeles, just after handing in the thesis, he never had an opportunity to condense it for publication. This duty was therefore performed by the instructor, D. L. Webster, with whom he had done the research, but from whom only very little help was ever needed by such an original and able man as Paul Wagner.

I. Introduction

LITTLE work has been done on secondary electron emission at voltages ranging from 16 to 40 kv. At lower velocities, 10–12,000 volts, investigation has been carried on by Becker[1] (10–1,000 volts) and by Stehberger[2] (1,000–12,000). Both used the opposing field method. Plotting against the opposing voltage the number of secondary electrons having energy enough to overcome it, Becker obtained, for lower primary velocities, curves of the following general characteristics: for opposing voltages from zero to about 36 volts there is a rapid falling off in intensity; as the opposing voltage reaches higher values the intensity decreases gradually and uniformly, and at an opposing voltage equal to the primary voltage it suddenly drops to zero. This led Becker to distinguish between three types of electrons involved in the process of secondary emission; these he called "secondary" electrons,

[1] A. Becker, Ann. d. Physik **78,** 228 (1925).
[2] K. H. Stehberger, Ann. d. Physik **86,** 825 (1928).

"rediffused" electrons and "reflected" electrons. This classification was accepted by Stehberger. The distinction between secondary and rediffused electrons was based by Becker on the fact that his curves are straight from about 36 volts onward to primary voltages. Denoting by $N(V)dV$ the number of electrons having energies between V and $V+dV$, Becker's curves imply that $N(V)$ is constant except below 36 volts. This constant value gives the number of the electrons Becker calls rediffused; the excess over this, at voltages less than 36 volts, is composed of what he calls secondary electrons. The reflected electrons, finally, are those which have practically the primary energy.

Becker and Stehberger found that the upper limit of energy at which there is an appreciable number of what they call secondary electrons is 36 volts, whatever the nature or thickness of the target and whatever the primary voltage (within the range stated above). They concluded that these secondary electrons are electrons of the target material knocked out by primary and rediffused electrons, that rediffused electrons are primary electrons which have suffered a large number of small encounters with an atomic nucleus. Becker finds that for higher primary velocities the number of reflected electrons diminishes. Stehberger, being unable to apply opposing fields up to the higher primary velocities, made the assumption that reflection completely ceases for these higher primary velocities, basing his assumption on Becker's results for lower velocities.

There is arbitrariness in Becker's distinction between secondary and rediffused electrons, for we are not at all assured that the number of rediffused electrons does remain constant within the interval from zero to 36 volts. In this paper, therefore, the term "secondary" will be used from now on in a broader sense, denoting all the electrons coming from a target bombarded by primary electrons.

M. Baltruschat and H. Starke[3] find that for voltages larger than 6,000 volts the number of fast electrons increases, and that at 30,000 volts even 80 percent of them possess velocities of the order of magnitude of the primary velocities.

Chilinsky[4] did some work on the magnetic velocity spectra of secondary electrons produced from silver by primary electrons of 5 to 20 kv, and found that most of outgoing electrons had velocities about 0.8 of the primary value, and that the intensity in the spectrum fell off sharply at about 0.9 of the primary velocity.

Egon Lorenz[5] carried on investigations, on the x-rays from the back of a tungsten target. He covered a wide range of voltages, up to 83 kv, and compared the spectrum of this so-called "stem-radiation" with that of the focal-spot radiation. The spectra are similar, but the entire stem-radiation spectrum is displaced, towards longer wave-lengths. Thus it approaches the axis at a point which is displaced from the short-wave limit of the focal spot.

[3] Baltruschat and H. Starke, Phys. Zeits. **23,** 403, (1922).
[4] S. Chilinsky, Phys. Rev. **28,** 429 (1928).
[5] Egon Lorenz, Zeits. f. Phys. **51,** 71 (1928).

Beyond this point, it is true, there is a weak intensity extending as far as the focal spot limit, but Lorenz attributes this small amount of radiation to general scattered rays. He then interprets the apparent short-wave limit of the stem radiation by the hypothesis that the primary electrons eject electrons from the L (or other) levels of the target atoms, and that these secondary electrons cause the stem radiation; the short-wave limit of the focal-spot and stem spectra would then differ by just the frequency corresponding to the amount of energy required to extract these electrons. For instance Lorenz observes that at 22.4 kv primary voltage this difference in energy or voltage corresponds to the M level; and at 83.3 kv, to the L level. He states that this can be explained by the known fact "that the greater the energy of rays, the larger is the proportion of them absorbed in higher levels of any series in comparison with that in the other levels." Lorenz concludes that, if the primary cathode-ray energy is about 40 times that of, say, the M level, absorption would cease in that level and proceed to the next higher that is, the L level.

If Lorenz's explanation of his data is correct, it demands revision of current ideas on some other points. Each L electron ejected as a secondary electron must leave an L vacancy in an atom at the focus, and the filling of this vacancy will often, if not usually, cause the emission of a quantum of x-rays of one of the L lines. At 83 kv, an L quantum from tungsten carries off only about a tenth of the energy brought into the focus by the primary cathode ray, and the percentage of L vacancies causing L quantum emission may not be over 50 percent. Even so, however, if the number of secondary electrons is 20 or 30 percent of the number of cathode rays, and if they are chiefly from the L levels, we should expect 1 or 2 percent of the cathode ray energy to reappear as L-series radiation from the focus, as a result of the ejection of only such L electrons as escaped from the target, and much more as a result of the ejection of other L electrons not so directed as to leave the target. This is a considerably greater amount of energy than the total radiation from tungsten at 83 kv (about 0.75 percent). Thus this comparison, and also comparison with other data on line-emission efficiencies,[6] lead to serious doubt about the hypothesis that many of the high-speed secondary electrons are ejected L electrons.

However, some of the secondary electrons must be of this type, and a further test is needed. For this purpose, the magnetic velocity spectrum suggests itself, and the next question is what to look for in it.

The secondary-electron velocity suggested by Lorenz's stem-radiation spectra, at least as a maximum, is that which would occur if all the kinetic energy possessed by a cathode ray as it enters the target is transferred to an L electron, which then loses only enough energy to escape from the atom. Most ejected L electrons, however, should have less kinetic energy than this maximum, for two reasons. First, most of the atoms from which the L electrons are ejected are not at the surface of the target, and there are energy

[6] D. L. Webster, Proc. Nat. Acad. of Sci. **14**, 330 (1928). Data here indicate that when an 80 kv. electron strikes a block of silver, it has a line-emission efficiency of only about 0.1 percent.

losses along the paths of both the primary and secondary electrons. And second, in the act of ejection, the cathode ray should probably not transfer all its energy to the L electrons. It may be possible to eliminate the former of these causes for deficiency of energy, if the target can be made thin enough, but the latter is inherent in the atomic process. Thus even with an infinitely thin target, the energy limit described above might at best be looked for in the velocity spectrum only as a discontinuity in the first derivative of the intensity; and with a thick target, only in the second derivative.

These predictions are somewhat discouraging, but not completely so. For even if the secondary electrons were of uniform velocity, like the primary, the discontinuity in the x-ray spectrum of the stem-radiation would still be only in its first derivative. And uniform velocity means, for the velocity spectrum, not simply a finite discontinuity in some derivative, nor even in the intensity function itself, but in its first integral. In general, the order of the lowest derivative in the stem-radiation spectrum, having a finite discontinuity, should be two units higher than that in the velocity spectrum. Thus the better of the two spectra, as evidence on the question in hand, should be the velocity spectrum, which ought therefore to be explored thoroughly. And regardless of all such hypotheses as are discussed above, such exploration will surely improve our understanding of the process of secondary electron emission.

II. Apparatus and Methods

The apparatus used here was of the well-known type for semicircular focussing of a magnetic spectrum, as described by Robinson,[7] and is illustrated in Figures 1 and 2. The source of the secondary electrons to be

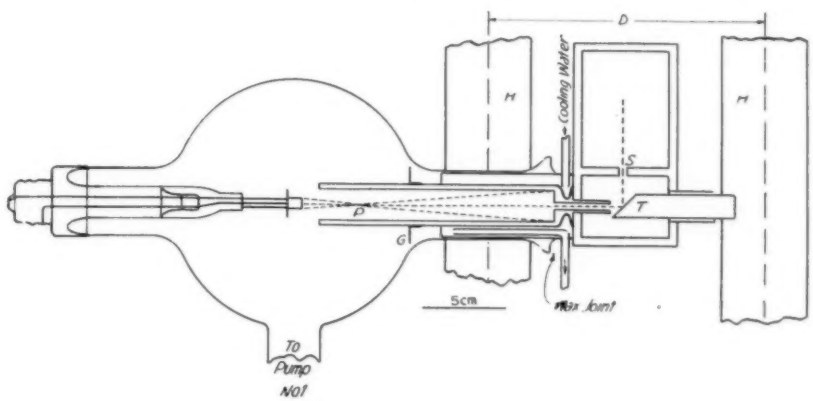

Fig. 1

analyzed into a spectrum is the target, T, shown from two directions in Figs. 1 and 2. The familiar magnetic focussing of the electrons is illustrated in Fig. 2, while Fig. 1 shows how the primary rays came along the lines of the magnetic field, as in Chilinsky's apparatus. Thus they travelled in straight

[7] H. Robinson, Proc. Royal Soc. **A104,** 455 (1923).

lines, from the Coolidge cathode in the glass bulb at the left, to the target T. The current producing this field ran in a pair of Helmholtz coils, indicated in Fig. 1 by the broken segments marked H. The brass box, in which the electrons made their semicircular paths, communicated with the glass bulb only through the very narrow slit S, and both of the chambers needed very good vacuum. Therefore, even though a test showed that the pump leading from the box alone would evacuate the bulb satisfactorily, a pump from the bulb was added as a precaution.

The target was sometimes a solid rod of aluminum as shown here, sometimes a brass rod with copper, silver, or gold soldered to it, and sometimes a brass tube, 7 cm deep, with a bore of 1 cm diameter, covered at the end with aluminum, silver, or gold leaf, to make a thin target. In each case, the primary rays struck the target at 45°, and the secondary rays used left it at the same angle, being thus 90° from the primary. The thicknesses of the thin targets were: Al 0.53×10^{-4} cm, Ag 0.18×10^{-4} cm, Au 0.23×10^{-4} cm.

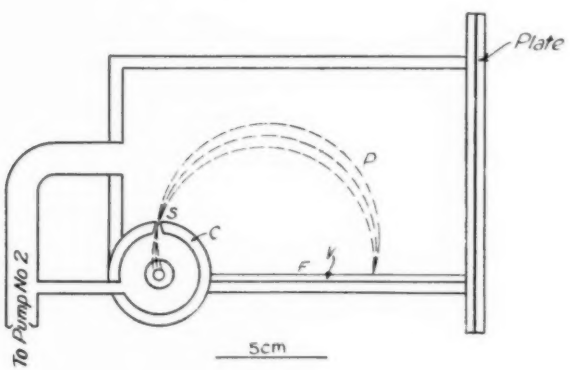

Fig. 2

Some other numerical data were as follows: slit S, 1.4 cm by 0.025 cm; diameter of hole through which the cathode rays approached the target, 0.2 cm; fraction of the cathode rays going through this hole, about 5 percent; radius of the Helmholtz coils, 17 cm; center of whole Helmholtz coil system, at the center of an electron path of radius 5 cm; non-uniformity of field (by test coil) not over 0.9 percent from its value at the center, anywhere on a radius of 6 cm.

The voltage applied to the primary cathode rays was obtained by connecting the cathode to the negative line of the D.C. system of the laboratory, and the brass box to the neutral line, which was grounded. It could be held constant to better than 0.3 percent, and the fluctuations due to the primary A.C. were far less than this.

For final use, spectra were photographed at four voltages, 16, 20, 30, and 40 kv, the first two with 1 ma (of which, as noted above, only about 5 percent reached the target), and the last two with 0.6 ma. To insure constancy of voltage and magnetic field in each exposure, the following procedure was adopted. First, the film was inserted, the box closed, and the ap-

paratus pumped to a high vacuum. Second, the current in the Helmholtz coils was set for a value such as to deflect secondary electrons of primary velocity into semicircles of 5 cm radius, and it was watched carefully thereafter. Then the high voltage was turned on, adjusted, and watched by another observer, usually Mr. B. G. Eaton, to whom hearty thanks is due for the care with which he rendered this assistance. Third, the filament was heated gradually, taking about half a minute to heat, so as to avoid voltage disturbances due to slight evolution of gas, and it was maintained at the right temperature for 5 minutes. Finally, the filament current was shut off, then the high voltage, and last the magnetizing current. Thus all the electrons had a primary voltage and deflecting field, each uniform to 0.3 percent, so that no discontinuity in the magnetic spectrum could be blurred by any lack of constancy involving energy changes as great as 1 percent.

Beyond tests for discontinuities, however, this work is purely qualitative although the conditions of exposure and development of the films were kept as constant as possible, to facilitate the comparisons of films. Especial care in this respect was applied to pairs of films, for thick and thin targets of the same metal at the same voltage, which were developed together.

Along with all the ordinary sources of photographic errors, it was unfortunately not found possible to eliminate entirely the effect of stray light from the filament. Tests without high voltage, however, (thus omitting the cathode rays) showed that the most serious fogging by such light occured only in the low-velocity region. In the high-velocity region, say above half the primary ray energy, where most of the secondary electrons appeared, the fog was very light and practically constant. Thus, fortunately, it can be neglected in discontinuity tests or in qualitative comparisons confined to this high-velocity part of the spectrum.

III. Results

Some densitometer graphs, comparing thick and thin targets of Al, Ag, and Au are shown in Figs. 3, 4, an 5 respectively; and some for thick targets only, of Al, Cu, and Au, in Fig. 6.

As will be seen on inspection of these graphs, *all these spectra are continuous.*

With regard to discontinuities in the derivatives of density or number of electrons with respect to velocity, it is evident that *there is apparently a real discontinuity in the first derivative, in every spectrum, at its high velocity end which is always found on measurement to occur at a velocity equal to that of the primary cathode rays. Aside from this point, however, no discontinuities have been found.*

First-derivative discontinuities would of course be much easier to detect than second, of the same relative proportions. Considering now only the thick targets, it has already been noted that we cannot expect to find any evidence of electrons ejected from the inner orbits, except in second-derivative discontinuities. Therefore, so far as we can tell here, such electrons may constitute several percent of the secondary electrons. But if they con-

stituted a majority, it would be a different matter. If, for example, in gold at 20 kv the majority of the secondary electrons were ejected from the M

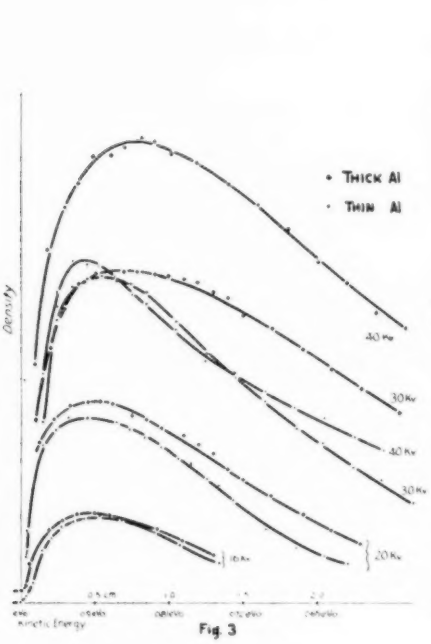

Fig. 3

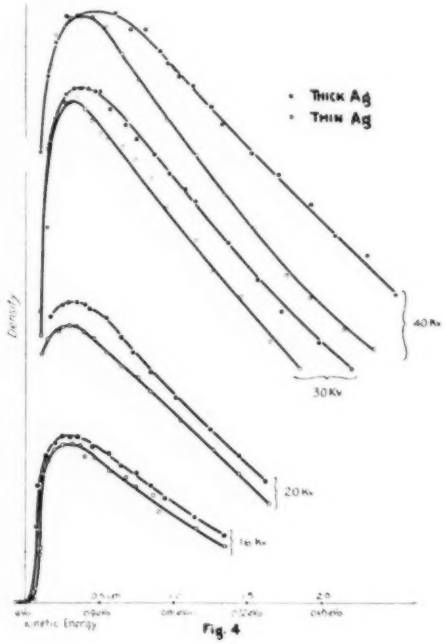

Fig. 4

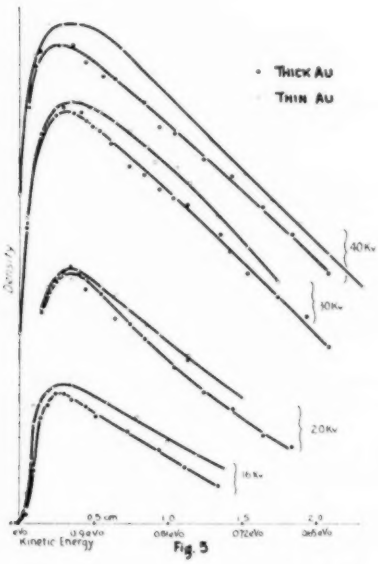

Fig. 5

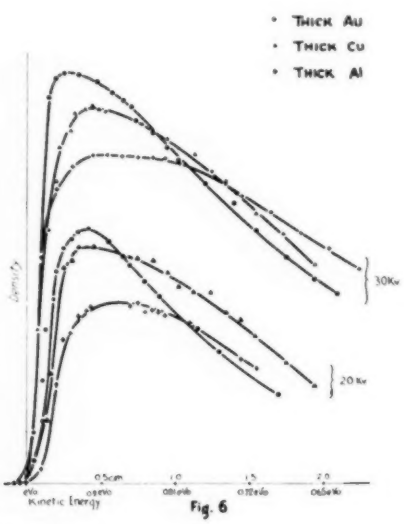

Fig. 6

Figs. 3, 4, 5 and 6

levels, we should expect to find relatively few electrons of energy greater than $(20-4)$ kv, or $0.8eV_0$, and just below this energy we should expect the density to begin to increase rapidly. The facts, however, are totally different

from any such prediction, not only in this spectrum, but in all the spectra. We must, therefore, conclude that, although some of the secondary electrons undoubtedly do arise from ejections from the inner orbits, they are a very small minority.

Turning now from discontinuity tests to qualitative information on other matters, still on thick targets, we find for all these elements, Al, Cu, Ag, and Au (as Chilinsky found for Ag up to 20 kv) that most of the high-speed secondary electrons have very high speeds. In terms of kinetic energy the maximum densities in these spectra occur at energy values bearing nearly constant ratios to the primary energy, eV_0. For Al, this optimum energy eV_m is about 0.85 eV_0; for Cu, about 0.90 eV_0; for Ag and Au, each about 0.94 eV_0. The probable errors in these ratios are several percent, of course, especially for Cu, for which relatively few photographs were made.

Below the optimum energy, in every case, the density declines rapidly, reaching half its maximum somewhere around 0.6 or 0.7 eV_0. Part of this decline may result from a decline in the photographic effect per electron, though not if each electron causes development of one grain, as may be possible. These statements on densities give, of course, only a qualitative idea of the laws governing the number of electrons per unit energy interval, but this number must vary in a manner roughly similar to these densities.

Since the conclusions drawn here differ radically from those of Lorenz, a question arises, whether the difference is due to theoretical assumptions in the interpretation of the data, or to some hidden source of experimental error. From the present data on the velocity spectra of the secondary electrons, we may predict roughly the form of the x-ray spectrum of the stem radiation they might excite. Considering only gold, as the element most like Lorenz's tungsten, the outstanding feature is the concentration of the secondary electrons in the general region around 0.9 eV_0, ± 0.1. The x-rays due to such electrons would not be expected to show any very sharp short-wave limit, but the general form of their spectrum would be much like that of the x-rays from the focal spot, except that it would be shifted to wave-lengths about 10 percent longer, and blurred out by ± 10 percent, more or less. Considering the short-wave limit more carefully, what it should show, as noted above, is a finite discontinuity in a derivative of order two units higher than that of the discontinuous derivative in the velocity spectrum. Therefore, since the velocity spectrum has its discontinuity in its first derivative, the x-ray spectrum should start, as measured from its short-wave limit, more or less like the curve $y=x^3$. In other words, it should have a graph which runs very low near the limit, and curves upward rather sharply at a wave-length somewhat greater. It is, therefore, not inconceivable that this sharp upward curvature might occur in the region where most of the secondary electrons would have their individual short-wave limits, that is, around 10 percent above the true short-wave limit. This is just about the region where Lorenz found a strong upward curvature in each of his spectra, assuming it to be a short-wave limit and assuming the weak radiation of still shorter wave-lengths to be stray rays from the focal spot. Thus

it may well be that the only cause for difference between his conclusions and the present lies in these assumptions, and that the data are consistent within the limits of reasonable experimental errors.

Turning now to the thin-target velocity spectra, they prove somewhat disappointing. Differences from the corresponding thick-target spectra are found only in Al and Ag, and there only above 20 kv. However, some recent theoretical work by Bothe,[8] on the stoppage of cathode rays in matter, throws light on this point. In thick targets, only very few cathode rays are stopped far short of their normal range, by large losses of energy; but practically all of them are deflected by nuclear attractions without much energy loss, in very short distances. Thus, at the speeds used here, they have completely lost all sense of direction before they have gone a micron. Qualitative calculations on rather loose assumptions related to those of Bothe, make it quite reasonable to expect many of the cathode rays deflected back out of the metal to have had very short paths within it. Such deflected cathode rays (or rediffused, as Becker would call them) should therefore have two characteristics in common with the secondary electrons observed here: first, that each electron should retain a large fraction of its initial kinetic energy; and second, that a metallic film, whose thickness is small compared to the range of a cathode ray in the metal, should nevertheless be thick enough to give practically the same velocity spectrum as a thick target. The agreement of theory and observation here tends to confirm the view that most of these high-speed secondary electrons are rediffused cathode rays.

With regard to how thin a target must be, to give "single scattering," and really give the velocity spectrum of an infinitely thin target, it seems probable that this requirement of thinness is considerably more severe than that for obtaining a "thin-target" x-ray spectrum. For velocity spectrum work, these spectra show that 0.2 micron gold is "thick" even at 40 kv; likewise 0.2 micron silver and 0.5 micron aluminum are each thick at 20 kv. To consider such films really "thin" from this viewpoint, these voltages must be greatly exceeded.

[8] W. Bothe, Zeits. f. Physik **54,** 161 (1929). Mr. Wagner had not seen Bothe's work, but this application of Bothe's theory tends to confirm the views Mr. Wagner expressed, as to the origin of the secondary electrons, and is therefore a reasonable extension of his paper.

ELECTRODYNAMIC DAMPING IN PULSATING STARS

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(Received November 29, 1929)

Abstract

Small radial pulsations of stars are shown to be highly damped by electrodynamic forces when the star has a magnetic field unless the star is very diffuse. The author's theory of the permanent magnetic field of the sun indicates that the field is produced by regenerative means which is initiated by a small field arising from some more fundamental mechanism. The small initial field is probably produced by the rotation of the star combined with a separation of charge, although it may conceivably arise in other ways. Thus rotating stars will have a magnetic field and cannot pulsate, and conversely stars which pulsate can have no magnetic field and probably do not rotate. This is in accord with the idea that Cepheid variables, being youthful giants, are so large that they would be unstable under rotation. These considerations appear to remove the difficulties encountered by Eddington in his detailed theory of star pulsations.

A CLASS of stars known as Cepheid variables are observed to go through regular periodic changes in their brightness, color and spectrum. It appears that the variation must be due to a variation of surface temperature rather than to eclipses or a rotation of the star, for observation shows that the rise in surface temperature is much more rapid than its decline. The astronomical observations are well explained by the pulsation theory which was first proposed by Shapley and later worked out in detail by Eddington.[1] This theory attributes the observations to a periodic radial expansion and contraction of the star under the joint action of gravitation, radiation and gaseous pressure. In this theory it is supposed that a star is in internal equilibrium and that the pressure at any level due to the weight above it is just balanced by the outward gaseous and radiation pressure. Let the entire star be uniformly compressed. On removing the constraint the internal radiation and gaseous pressures will expand the star and the inertia of the moving material will cause it to expand beyond its equilibrium position. This may give rise to an oscillation which can be sustained if energy is supplied in phase with the variation and if it is of sufficient magnitude to overcome the dissipative forces. Eddington has examined the problem and finds that if the pulsation of Cepheid variables is to be explained satisfactorily nearly all stars should pulsate and the phenomena should be more generally observed than is actually the case. In the treatment of the subject of star oscillations no account has been taken of electrodynamic forces and as we shall see presently these forces may be large and always act in such a manner that they tend to damp out very rapidly any radial oscillation of a star.

[1] Eddington, Internal Constitution of the Stars, Cambridge Press (1926).

Indeed, the present paper shows that radial oscillations of a star can exist only under very special conditions; conditions which appear to be satisfied in the youthful giant stars.

In an earlier paper[2] the writer outlined a theory of the origin of the magnetic fields of the sun and earth. The theory showed that any highly ionized star having radial temperature or gravitational symmetry would be expected to build up a large magnetic field by regeneration if a small initial magnetic field were present to start the regenerative process. All stars possess the requisite radial temperature and gravitational symmetry and it is only necessary to produce a small initial field to bring about their complete magnetization. The small initial field might be attributed to a "magnetic collision" with the stray magnetic field of another star or in some other way. Earlier work on the sun[3] indicates, however, that a star's magnetic field is more or less confined by the diamagnetic action of the ions in the stars atmosphere which execute long free paths. It seems more reasonable to consider the initial field as arising from gyromagnetic effects or from the gross rotation of the star combined with a slight gravitational or thermal separation of charge. Such an assumption leads to the correct sign for the magnetic field of the sun and earth. The general conclusion is that any star which possesses appreciable angular momentum will be magnetized. We must therefore examine what effect a magnetic field may have on the stability of a star and in particular we shall examine the effects produced by the magnetic field when the star is subject to a small symmetrical radial oscillation.

Assume for simplicity that the magnetic field inside a star is uniform and consider the forces acting on a ring of star material which lies in a plane perpendicular to the magnetic field and which expands and contracts radially with the star itself. In order to keep the essential physics before us let us also assume that the ring has a mean equilibrium radius R_0 and that any expansion or contraction of the ring will set up elastic restoring forces which are proportional to the displacement of the ring from the equilibrium position. On account of the symmetry we may describe the process by writing down the equations of motion for the material enclosed by unit volume of the ring. In addition to the inertial and elastic forces, account must be taken of the dissipative forces and in the following we shall consider only those of electromagnetic origin. Consider an expanding ring of star material. As the ring expands the magnetic flux enclosed by the ring is increased and an electromotive force is induced. This electromotive force produces a current in the closed circuit of the ring which is always in such a direction as to oppose the motion. Suppose the ring is expanding outward with a velocity V. Then the electric field E produced by the motion is

$$\boldsymbol{E}=\boldsymbol{V}\times\boldsymbol{B} \tag{1}$$

where **B** is the constant impressed magnetic field intensity of the star. The force **F** acting on unit volume of material is by aid of (1)

[2] Gunn, Phys. Rev. **34**, 335 (1929).
[3] Gunn, Phys. Rev. **33**, 614 (1929).

$$\boldsymbol{F}=\boldsymbol{i}\times\boldsymbol{B}=\sigma(\boldsymbol{V}\times\boldsymbol{B})\times\boldsymbol{B} \tag{2}$$

where $\boldsymbol{i}$ is the current density and σ is the conductivity. For the purposes of the rough calculations in this paper the classical expression for conductivity can be used and Eq. (2) reduces (in the special case where the ring expands in a plane perpendicular to the impressed magnetic field) to

$$\boldsymbol{F}=-\sigma B^2\boldsymbol{V}=-\frac{Ne^2\lambda B^2}{2(3mkt)^{1/2}}\boldsymbol{V} \tag{3}$$

where N is the number of ions per cm^3, e the ionic charge (e.m.u.), λ the mean free ion path, m the mass, k the Boltzmann constant and t the absolute temperature. It has been shown previously[4] that the expression for the electrical conductivity given by Eq. (3) breaks down and the conductivity decreases greatly when the mean free path of the ion approaches (in numerical value) the radius of the circle generated by the ion as it spirals about the impressed magnetic field. It has also been shown[3] that in the outer surface layers of the sun the mean free paths of the ions are longer than this critical radius and the conductivity of the region low. Thus the currents flowing in a very diffuse star or in the outermost layers of the star are small and the resulting damping is probably unimportant.

If we measure r from the equilibrium position of the ring, the equation of motion for a typical volume element is

$$\rho\frac{d^2r}{dt^2}+\sigma B^2\frac{dr}{dt}+K^2r=0 \tag{4}$$

where ρ is the density of the star material and K^2 is a constant which must be determined by a complete analysis or by observation of the free period of oscillation. With $2u=(B^2\sigma/\rho)$ and $v^2=K^2/\rho$ the solution of (4) is of the form

$$r=C_1e^{[-u+(u^2-v^2)^{1/2}]t}+C_2e^{[-u-(u^2-v^2)^{1/2}]t} \tag{5}$$

and may represent a completely damped pulse, a critically damped oscillation or a free oscillation depending on the value of the coefficients. From Eq. (5) it is seen that any mean displacement will be reduced to roughly one e^{th} its initial value in a time

$$t=\frac{1}{u}=\frac{2\rho}{B^2\sigma} \tag{6}$$

and if the system is oscillatory it will oscillate with a frequency

$$f=\frac{1}{2\pi}\left(\frac{K^2}{\rho}-\frac{B^4\sigma^2}{4\rho^2}\right)^{1/2}. \tag{7}$$

It will be noted in passing that the frequency of oscillation is sensitive to changes in the value of B, for σ will have fairly large values in any ordinary

[4] Gunn, Phys. Rev. **32**, 133 (1928).

star. It must be remembered that Eq. (6) only applies to rings which expand at right angles to the magnetic field. In all other orientations the damping will be somewhat less and there is a tendency for the star to expand more at the magnetic poles than at the equator. In fact, closed circuits in a plane containing the magnetic axis might be expected to produce no damping of the type we have considered. Moreover, certain types of oscillation can be conceived wherein any typical current ring suffers no change in area but takes on successive elliptical forms. Such an oscillation would induce no current and electrodynamic forces would not be important.

It will be necessary to consider an actual case to determine the importance of electrodynamic forces. The only star which we definitely know possesses a magnetic field is the sun and earlier work,[2,3] has indicated that its internal magnetic field intensity was not less than 10^4 gauss. We shall apply a disturbing force to the sun in such a manner as to set it in radial oscillation and calculate by Eq. (6) and (3) the time it will take the oscillation to die out. We will take representative values of the quantities as follows:

$B=10^4$ gauss	$\rho=1.4$ gm/cm^3	$N=10^{23}$ ions/cm^3
$e=1.59\times10^{-20}$ e.m.u.	$\lambda=10^{-6}$ cm	
$m=10^{-27}$ gms	$k=1.37\times10^{-16}$	$T=10^7$ degrees

which leads to a value of $\sigma=6.25\times10^{-6}$ e.m.u. Thus by Eq. (6) the time for the mean solar displacement to be reduced to 1 e^{th} of its initial value is 4.5×10^{-3} seconds. It is therefore clear that no oscillation can take place and the sun is in stable equilibrium. It must be emphasized that this conclusion is only true for small oscillations which produce no appreciable change in the impressed magnetic field. When the oscillations are large the problem offers mathematical difficulty but qualitatively it appears that large oscillations would be damped out much less rapidly than small ones and that the surface layers will reach equilibrium well before the deeper ones. If it is assumed that the numerical values which have been chosen in the case of the sun are representative of stars in general, it is doubtful if any star having a magnetic field can oscillate over any extended period of time. We must therefore interpret the occurrence of true pulsating stars to mean that the star does not have a magnetic field or that it is so diffuse that the ion free path is long and the magnetic field reduces the electrical conductivity almost to zero.

The writer's theory of the origin of the permanent magnetic fields of the sun and earth is based on a regenerative action which requires a small initial magnetic field to trigger it off. The small initial field is most simply accounted for by a rotation of the star and it seems correct to assume that every rotating star is highly magnetized. Conversely, a star which has no magnetic field would not be expected to rotate. The foregoing considerations definitely suggest that a true pulsating star does not rotate. Appeal to observation shows that all the stars that are suspected of being true

pulsating bodies are youthful giants which astronomers believe would break up if they were possessed of any great amount of angular momentum. This observed fact seems to bear out the conclusion that true radial pulsation of a star is possible and the argument shows that the existence of such entities in the universe does not necessarily mean that all stars should be unstable and exhibit a radial pulsation.

Jeans[5] has concluded that the pulsation theory is inadequate to explain the observations and chooses to think of the variables as stars in the process of breaking up to form binary systems. Consideration of electrodynamic damping might be favorable to this theory if it can be shown that the probability of rotation for a star is very much greater than the observed probability for the occurrence of a nonpulsating star. Unless some such statistical relation be extablished the considerations of this paper appear to support the ideas of Shapley and Eddington as formulated in their pulsation theory. While it is too early to decide whether the present considerations support or disprove the pulsation theory of Cephied variables, it appears that electrodynamic forces play an important part in stabilizing a star and they must be considered in any complete study of its history. The possibility that electrodynamic loading of the type we have considered may account for certain observed features of Novae is now being investigated.

[5] Jeans, Astronomy and Cosmogony, Cambridge Press (1928).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Effect of Red Light on Stopping Potentials of Photoelectrons Liberated by Blue Light

In "Naturwissenschaften" (**41,** 806-807, October 11, 1929) was published a note by Erich Marx, announcing observations which seemed to show that red light superimposed on blue light falling on a photoelectrically sensitive potassium surface had the effect of decreasing the maximum kinetic energy of emission of the electrons liberated by the shortest wave blue light. This is a most surprising and important result, if true. Details of the experiment were missing, but the only care necessary to observe this effect seemed to be that of preventing light from striking the anode directly or indirectly while determining the stopping potentials of the photoelectrons. In fact, Marx explained that the phenomenon was easily observed qualitatively, on any commercial potassium cell.

Now, since most commercial model photoelectric cells are of the central anode type and require upwards of a hundred volts, at least, to produce saturation of the photoelectric current, shifts ranging from a fraction of a volt to a few volts in the voltage-current relation can only be detected at a voltage where the current approaches zero. Hence, it is undoubtedly at the foot of the stopping potential curves that Marx claims to have observed the effect of the red light superimposed on the blue. But, as rather carefully pointed out by Millikan [Phys. Rev. **7,** 18, 355 (1916)] and quite generally proven by experimental results, this part of the curve for a given anode is not a function of the cathode at all and can only be affected by a change in light frequency. Certainly there exists no sound reason for only the highest frequency of the incident light being altered, so the so-called "new photoelectric phenomenon" of Marx is hard to reconcile with experience or theory.

Such an apparent reduction of the retarding potential as cited above, however, would be produced if some of the incident or reflected light fell on an anode sensitive more to red light than to blue, and it seems highly probable that such was the case. For, in the first place, Marx stressed the importance of preventing light from falling on the anode, a precaution unnecessary if the anode were not light sensitive and one practically impossible to put into effect. In the second place, it is a matter of common observation that the anodes of potassium photoelectric cells frequently respond better to red light than the cathodes, a fact which suggested to Campbell [Phil. Mag. **6,** 633 (1928)] a method of making red-sensitive potassium cathodes. Undoubtedly the sensitivity of the anode to red is due to a thin film of potassium spontaneously deposited thereon, and these films naturally respond to light of longer wave-length than the bulk metal or heavy layer of the cathode [Ives and Olpin, Phys. Rev. **34,** 117 (1929)]. Whenever potentials are applied to retard electrons released at the cathode they accelerate at the same time any electrons liberated from the anode, and the measured current will be the difference between the number of electrons reaching and leaving the cathode. Since potassium, in bulk form or thick layers, responds well to blue light but not to red light, whereas potassium in the form of thin films on metals, responds well to red light, it is at once evident that if any scattered light fell on the anode, the presence of red light will occasion a greater reverse current and consequently the voltage at which the current becomes zero will be less than for blue light alone.

In order, therefore, to make a complete check of the "Marx phenomenon," a cell having an anode absolutely insensitive to

light should be used. I had available such a cell, made by preparing the cathode in a separate chamber and then slipping it into place within a nickel anode coated with soot. The cathode was not coated with potassium but with sodium, sensitized by the introduction of small amounts of sulphur and oxygen until the response to red light was far greater than that of potassium-hydride cells [Olpin, Abs. 57, Bull. Am. Phys. Soc. vol. 4, No. 2 (April 6, 1929) Phys. Rev. **33**, 1081 (1929)]. These alterations from the Marx experiment may be criticized, but there seems to be no reason for expecting potassium to behave differently from sodium in the property under discussion, unless it be the fact that potassium is far more likely to pass by vaporization to the anode than is sodium. The blue light was produced by inserting No. 49-EK Wratten filter in the path of radiations from a tungsten filament, and the red light similarly produced by using a No. 29-Ek Wratten filter. The photoelectric currents were read on a high sensitivity Leeds and Northrup galvanometer.

The results of this test are shown in Fig. 1. There was absolutely no effect of the red light on the electrons emitted with maximum kinetic energy, but an increase in the number of slower electrons. The voltage-current curve for both red and blue light falling simultaneously on the surface was exactly the sum of the voltage-current curves for the two colors of light used separately. This was found to be equally true when yellow light was used in place of the red.

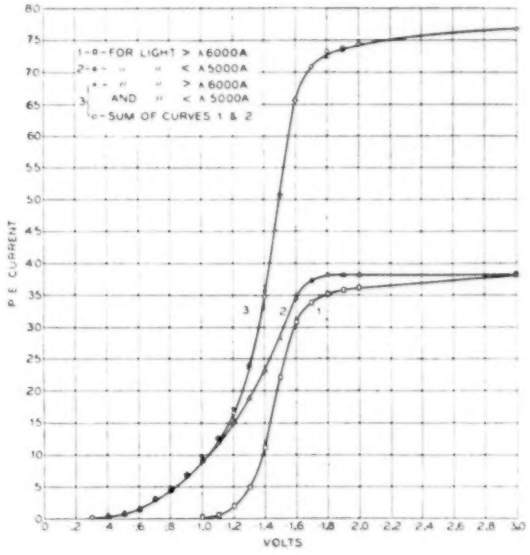

Fig. 1.

A. R. Olpin
Bell Telephone Laboratories, Inc.
New York, New York,
December 5, 1929

The Origin of Snowflakes

Experiments begun in 1920 on the conditions governing the origin and growth of snowflakes have now met with some success. It has been found possible to produce an opalescent cloud of snowflakes, to put individual particles of this cloud under microscopic observation within about five seconds of their inception, and to control their growth up to a diameter about four times that at which their outlines become distinguishable.

The experimental method consists in passing a current of cold dry gas—obtained by the evaporation of liquid oxygen or liquid air—into a mixing tee where it may meet a current of air and saturated water vapor supplied at a temperature a few degrees above 0°C.

The mixture passes immediately into the top of a vertical observing chamber kept at a few degrees below zero, thence down through the chamber and out by horizontal lateral passages. The bottom of the chamber is made of a glass plate with a fine scale engraved or etched on its upper surface. A microscope objective under the plate is placed so as to form a magnified image of the scale and of any deposit that may occur on it, in the focal plane of an eyepiece or on a photographic film. Illumination is downward through the observing chamber. With these arrangements, the admission of the moist air to the mixing tee is accompanied by a reddening and darkening of the field of view, and in a few seconds the glass receives a deposit of particles of the order of 5×10^{-4} cm in diameter—too small to permit observations on their shape with the optical system used. An additional supply of vapor to the chamber results in the visible and rapid growth of these particles to sizes which display definite outlines. Diameters of 2×10^{-3} cm are frequent. The particles thus grown may be held under observation for a minute or more, and photographed.

After the process of growth has started, it is not possible to bring onto the plate an additional deposit of particles of the original size. The opalescence occurs as usual, but produces only a further growth of the particles already on the plate. This indicates that snowflakes, like raindrops, grow at the expense of their smaller neighbors, and implies that the equilibrium vapor pressure above a particle of ice decreases with increasing dimensions. The opposite effect has been observed by Farnsworth [Phys. Rev. **34,** 684 (1929)] in the case of small copper crystals growing at the expense of a large one.

The crystalline character of the deposit is obvious from an inspection of the photographs. Many of the particles show twinning, and a few appear to be aggregates. More common than either of these are forms without internal markings, perfectly transparent, revealing in their outlines the symmetry characteristic of the hexagonal system. The symmetry is not merely that of external form, for when these crystals are made to grow, each of the six faces advances at the same rate, so that the outline remains similar to itself. This observation indicates that the faces are alike in physical properties, and that therefore the particles are monocrystalline. The deposits also contain abundant material for the study of the so-called cubic crystals which have been reported occasionally by observers of naturally formed ice crystals.

The method is probably applicable to the formation and growth of small single crystals of substances other than water, and affords a means of studying problems of crystal structure in the light of the kinetic theory.

JOHN MEAD ADAMS
Department of Physics,
University of California at Los Angeles,
December 10, 1929.

Inhomogeneities in Crystals

Ever since Griffiths proposed the existence of internal flaws in apparently perfect crystals as an explanation of certain anomalies in their behavior, various workers have attempted experimental verifications of this hypothesis. There have likewise been attempts to justify it on theoretical grounds and thus bring it within the domain of regular and predictable phenomena.

The subject derives its importance from its bearing on the validity of some highly fundamental physical measurements. Among these are the refined determinations of compressibility such as those of Bridgeman and the determinations of x-ray wave-lengths based on the assumption that the calcite crystal is perfect and homogeneous. Other determinations affected are those of all elastic constants, thermal and electrical conductivities and densities. All the data of crystal energetics are subject to large and unpredictable errors if internal inhomogeneities exist.

Mehl and Canfield in a note (Nature, Sept. 28, 1929) have discussed the question of *voids* in crystals and conclude that the experimental evidence, particularly the recent measurements of x-ray wave-lengths with a ruled grating (Beardon, Proc. Nat. Acad. **15,** 6 (1929)) cannot be reconciled with their existence.

The most important recent paper supporting the inhomogeneity hypothesis is by Zwicky (Proc. Nat. Acad. **15,** 11 (1929)) who contends not for the presence of voids but for planes of altered density occurring at fairly regular intervals within the lattice and di-

viding it into a sort of mozaic. He has previously secured experimental evidence of such structure on the *surface* of etched metal crystals. The paper here referred to is devoted to a theoretical treatment of the subject, resulting in a prediction of the required phenomenon, and it is this to which the present writer wishes to take exception.

In setting out on his discussion the author makes (in substance) the following steps of reasoning:

Crystals in general contract laterally when they are elongated in one direction. Hence, if we picture the crystal as built up of planes of atoms, the withdrawal of neighbor planes permits the atoms of a given plane to come closer together. Hence the atoms of any one plane would draw nearer together if that plane were isolated and allowed to come to its equilibrium configuration.

This reasoning is fallacious. The elongated crystal is not in equilibrium, but has had work done on it by external forces; the configuration it assumes is determined by the condition that the work done by the external forces shall be a minimum. As a matter of fact the process of withdrawing the neighbor planes *pulls* the atoms of the given plane into closer proximity. A plane of atoms when isolated might expand or contract from its dimensions in the lattice, depending on the density of packing of the atoms in the plane. For example a (111) plane of a homo-polar face-centered cubic lattice would expand; a (100) plane would contract. Since the remainder of the proof rests on the argument already outlined it requires no comment. Although the reasoning is called thermodynamic, it is in reality dynamic, with the words "free energy" substituted for "potential energy."

As regards the experimental evidence, there can be little doubt that an actual mozaic structure does exist on the *surface* of a crystal. In fact the effect is to be expected as a result of the surface energy, as the present writer hopes to show in a paper now in preparation. But it must be emphasized that the experimental evidence now at hand establishes the existence of *surface inhomogeneities only*. The non-agreement of predicted tensile strengths with experimental values—the main prop of the mozaic argument—is susceptible of too many other explanations to serve as *prima facie* evidence of internal inhomogeneities.

R. H. CANFIELD

Naval Research Laboratory,
Bellevue, Anacostia, D. C.,
December 20, 1929.

A New Relativity Theory of the Unified Physical Field

I have succeeded in applying to the above question what appears to be an important new conception regarding the significance of relativity mathematics with noteworthy results. I have abandoned altogether the quasi-geometrical interpretation with such hazy notions as parallel displacement in a curved space of n dimensions. Instead, we construct an indeterminate vector field by means of Eddington's displacement rule (considered now as an association rule), and identify it at every point with the velocity a material particle might have if present there and then. Vector lines in this field are necessarily the orbits of material particles under any physical conditions.

We now construct an indeterminate tensor field, and by its means define the invariant magnitude of the elementary arc of these vector lines. Actual physical vector and tensor fields are necessarily determinate at every point, and these are defined as usual by applying the association rule round a closed loop. This gives the usual symmetric and antisymmetric field tensors.

When the antisymmetric field tensor vanishes the vector lines reduce to Einstein's so-called geodesics. The electric field is given by the antisymmetrical tensor, and here the vector lines become mathematically equivalent to the known orbit equations. Maxwell's first set of field laws are identically satisfied, and the set referring to electric charge and current are approximately true for small fields. In strong fields in the neighborhood of atomic nuclei the electron orbits reduce again to geodesics, independent of negligible radiation due to their acceleration, and Maxwell's second set of laws no longer holds. This is obviously very strong support for our theory. But further; the introduction of field laws which reduce to Einstein's in the pure gravitation field appear to lead to a principle of selection among the orbits in nuclear regions.

Before leaving England this summer, the

writer prepared a hurried account of the above theory intended for publication in the Proceedings of the Royal Society. It unfortunately gave no explanation of the mathematics which latter were faulty at one point. A careful and complete revision has now proved the soundness of the theory, and publication will follow as quickly as possible.

WILLIAM BAND

Physics Department,
Yenching University, Peking,
December 19, 1929.

The Microstructure of Some Magnetic Alloys of High Platinum Concentration

In a recent paper [Phys. Rev. **34**, 1217 (1929)] the writer has described an attempt to measure the magnetic properties of ferromagnetic atoms in a somewhat isolated state. The method used was to study alloys of platinum with a small percentage of cobalt. Alloys of 5% cobalt and 10% cobalt were both ferromagnetic. Provided these alloys are solid solutions, which was believed to be the case, the cobalt atoms in them could be regarded as mostly isolated from one another by the intervening platinum atoms.

A microscopic study of these alloys has since been made. The diagram of thermal equilibrium has not been obtained for the Pt-Co series, although Carter has investigated many high-platinum alloys and believes platinum and cobalt form an isomorphous series of solid solutions. However, it was necessary to be sure that two solid solutions did not exist together in a given alloy, with the result that a particular cobalt alloy would generally consist of a cobalt-rich phase plus a platinum-rich phase, or of a platinum-cobalt mixed crystal in pure platinum; in this case, increased platinum concentration would not mean further isolation of cobalt atoms, but a different proportion of the two phases.

Sections of each alloy were prepared, polished and etched with hot aqua regia. Wires in the hard-drawn state showed, under the microscope, that their crystals were elongated and distorted in the direction of strain. In the annealed state, however, each alloy showed the polygonal polycrystal pattern characteristic of pure metals or single solid solutions. If two phases were present in, say, the 10% cobalt-90% platinum alloy, they would have to exist in nearly equal proportions or one phase might be present in a small quantity between the grain boundaries. The 5% cobalt alloy, however, showed the same structure, although it, too, could not contain equal amounts of the two phases. In neither alloy was the characteristic eutectic structure of one phase imbedded in the other present. The sections were etched a little at a time and examined at each stage, but intercrystalline material was never detected. The sections etched uniformly, but the 5% cobalt several times more slowly than the 10% cobalt; as the acid more readily attacks cobalt, this again indicated that the cobalt atoms were distributed over all the crystals uniformly, the cobalt concentration in the 5% alloy being less throughout and the resistance to the acid hence greater. For comparison, a section of an annealed wire of pure platinum was similarly examined, and its microstructure was practically identical with that of the cobalt alloys. The alloys must, therefore, be solid solutions of cobalt in platinum, and the cobalt atoms in them isolated.

Platinum possesses a face-centered cubic lattice, while cobalt is hexagonal for lower temperatures and face-centered cubic at higher ones (about 600°C). As transformation points are generally rapidly lowered by alloying, e.g., the Curie point, these high-platinum alloys might be expected to have the cubic structure. High magnification (1300 times), revealed definite cubic formations in many of the crystals.

F. W. CONSTANT,
National Research Fellow.

California Institute,
Pasadena, California,
December 17, 1929.

Recombination of Electron and Alpha-Particle

The writers have computed by quantum mechanical means the probability of recombination between an electron and a hydrogen atomic ion or an alpha-particle, when the final state is the hydrogen atom or helium ion in some quantum state. The initial wave function used is that developed by Mott,[1] and represents a unidirectional

[1] Mott, Proc. Roy. Soc. **A118**, 542 (1928).

beam of electrons travelling toward a nucleus with velocity v. The final wave function is the usual one for the atom in one of its quantum states.

The matrix element of the moment corresponding to this transition is proportional to the target area of recombination, $q(v, \nu_i)$, discussed by Mohler.[2]

The calculations indicate that the target area for recombination of an electron and a nucleus of charge Ze is

$$q = 6.10 \times 10^{-11} Z^6 \frac{\exp\left[\pi k - 4k \tan^{-1}(1/k)\right]}{v\nu^2 \sinh \pi k}$$

where V is the electronic energy of motion relative to the nucleus in volts, ν is the frequency of the radiated light in wave-numbers, $k = 3.67\ Z/V^{1/2}$, and the final state is the normal state. This agrees remarkably well with the theoretical and experimental formulas given in the recent summary by Seeliger.[3] No approximations have been made in the derivation of this formula.

The q's for the upper states are similar expressions, none of them showing any maxima in the range of V between zero and infinity. Therefore the maxima obtained by Davis and Barnes must be due to some mechanism involving more than one electron and one alpha-particle. The explanation offered by E. Q. Adams[4] might be the correct one, despite Barnes's[5] objection. For the quantum mechanics indicates that processes not involving the electrical forces between the nuclei hold equally well for single nuclei, with the quantities giving the relative proportions of the resulting end products appearing as probabilities. In other words, if a stream of electrons falling on N alpha-particles creates n He^+ ions in time t, then when this same stream of electrons falls on one alpha-particle, there is a probability n/N that this one alpha-particle will become a He^+ ion in time t.

The authors have carried through this reasoning by probabilities from the beginning and have obtained an equation substantiating Adams's result. Since, however, the values of all the constants involved are not known, it is impossible to know at present whether this mechanism will account for the observed peaks.

E. C. G. Stueckelberg
Philip M. Morse

Palmer Physical Laboratory,
Princeton, N. J.,
December 15, 1929.

[2] Mohler, Phys. Rev. Supplement **1,** 217 (1929).

[3] Seeliger, Phys. Zeits. **30,** 354 (1929).

[4] E. Q. Adams, Phys. Rev. **34,** 537 (1929).

[5] Barnes, Phys. Rev. **34,** 1224 (1929).

BOOK REVIEWS

Müller-Pouillets Lehrbuch der Physik. 11 aufl. 2 band. Lehre von der Strahlenden Energie (Optik). 2 hälfte. 1 & 2 teil. KARL WILHELM MEISSNER, editor. Pp. xvi+xvi +929 to 2392. Figs. 625 to 1345. Friedr. Vieweg & Sohn, Braunschweig, 1929.

After some delay following the death of Dr. Lummer, the editorship of this standard text and reference work has been assumed by K. W. Meissner. Three times the bulk of the corresponding sections of the previous edition (1909), the new half-volume impresses one again with the rate at which the research workers in the field of optics have been outdistancing the publishers. The editor has carefully subdivided the field, and with the cooperation of several of the most able German physicists presents here a work thorough, well organized, and readable, that develops experimental and theoretical optics up to 1924–1925 and, in a few outstanding sections, further.

About a third of the space is given to spectroscopy, including chapters on spectroscopic apparatus and methods, by Meissner, Hettner, Czerny, and Gehrcke; series spectra, by Paschen; band spectra, by Kratzer; x-ray spectroscopy, by Coster; Zeeman effect, by Back; and the foundations of the quantum theory of atomic structure, by Pauli. The prospective reader who is led by the author's name and the publisher's date, to expect a unified present-day account of atomic theory in this last chapter, will be disappointed. There is an apology elsewhere (p. 1483) for this chapter, written in 1924, and there are excellent concise appendices on the introduction of the Goudsmit-Uhlenback magnetic electron and the fundamental work of Schroedinger and Heisenberg. But there is no sufficient excuse given for publishing, under the date 1929, of a good deal of obsolete material, in this chapter (e.g., Art. 11, Die Grenzen der heutigen Form der Quantentheorie) and others.

The older electromagnetic-optical phenomena are handled mainly by Buchwald and Ladenburg. Kohn has an exhaustive treatise on photometry.

J. E. MACK

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE CHICAGO MEETING, NOVEMBER 29 AND 30, 1929

The 159th regular meeting of the American Physical Society was held in Chicago, Illinois at the Ryerson Physical Laboratory of the University of Chicago on Friday and Saturday, November 29 and 30, 1929. The presiding officers were Professor Henry G. Gale, President of the Society, and Dr. W. F. G. Swann, Vice-President.

On Friday evening the Physical Society had a dinner at the Quadrangle Club. There were about one hundred members present. The after dinner speakers were Dr. W. F. G. Swann, Dr. Dayton C. Miller and Professor A. J. Dempster.

At the regular meeting of the Council held on Friday, November 29th, 1929, one was elected to fellowship, one was transferred from membership to fellowship, and one hundred and fifty-two were elected to membership. *Elected to Fellowship:* John B. Whitehead. *Transferred from Membership to Fellowship:* William V. Houston. *Elected to Membership:* T. E. Allibone, Emerson D. Bailey, William Baldwin Jr., E. G. Bangratz, LeRoy L. Barnes, Milton Bergstein, Arthur Bernhart, Donald K. Berkey, Luther M. Bingaman, Francis Birch, Heaton P. Blakeslee, Charles D. Bock, Gilbert F. Boeker, Isabel Boggs, Thomas H. Briggs Jr., Leslie E. Brooking, William F. Brown Jr., O. H. Caldwell, C. Wesley Carnahan, A. B. Carr, Randle V. Cartwright, Margaret L. Clark, Philip Constantinides, Trevor R. Cuykendall, Beryl H. Dickinson, James F. Duncan, J. R. Dunning, M. A. Easley, Sister Mary Edwina, Alexander Efron, Charles D. Ellis, John H. Findlay, Arthur W. Fleming, Hazel M. Fletcher, Arthur E. Focke, J. Franck, Austin R. Frey, Harold Q. Fuller, James W. Givens Jr., A. T. Goble, Martin Grabau, Newton M. Gray, John P. Hagen, August Hagenbach, Sigmund Hammer, O. Philip Hart, Charles D. Hartman, Alexander Harvey, Clifford E. Harvey, Edgar R. Hauser, Thomas Hazen, C. M. Hebbert, Jesse C. Hendricks, Willard H. Hickok, A. F. Horlacher, D. S. Hughes, Lewis H. Humason, Malcolm C. Hylan, H. F. Kaiser, Roy J. Kennedy, W. Jay Kennedy, James R. Kershaw, George E. Kimball, Harold L. Knowles, Matsui Kumiyasu, A. M. Kuethe, Olive M. Lammert, Charles C. Lauritsen, Glenn Q. Lefler, Lewis Larrick, Urner Liddel, Tate Lindsey, Erwin F. Lowry, Janet M. MacInnes, Homer E. Malmstrom, Louis Marick, D. E. Marshall, Tanaka Masamichi, F. A. Maxfield, Ronald L. McFarlan, R. T. McGoldrick, Edwin M. McMillan, Harold Mestre, Earl R. Miller, John S. Millis, Carol G. Montgomery,

Howard R. Moore, Neal D. Newby, J. L. Nickerson, Foster C. Nix, Will V. Norris, Helen B. Notestein, Leonard M. Onsgard, Herbert N. Otis, F. L. Partlo, John V. Pennington, William M. Pierce, Milton S. Plesset, Richard G. Poindexter, Wilson M. Powell Jr., Simeon A. Ratner, John J. Rheins, Charles E. Rich, Donald E. Richardson, H. P. Robertson, Walter W. Roehr, Harry Rolnick, Donald C. Rose, Jenny Rosenthal, Philip W. Rounds, Edward W. Samson, A. Sandow, S. P. Sashoff, Edwin G. Schneider, Harold F. Schwede, Raymond W. Sears, Shirleigh Silverman, William W. Sleator, F. Raymond Smith, John F. Smith, Letha A. Smith, David L. Soltau, Wayne T. Sproull, John R. Stehn, Louis Strait, Kuno Takuji, Tutomu Taraka, John B. Taylor, James S. Thompson, John A. Tiedeman, John S. Tobin, John W. Todd, A. H. Toepfer, Charles B. Vance, Robert J. Van de Graaff, Frank L. Verweibe, Alice M. Vieweg, Donald S. Villars, Worth Wade, Henry Walther, William H. Watson, Wayne Webb, Max Wehrli, Thomas W. B. Welsh, W.W. Wetzel, Mary A. Wheeler, John L. Wilson, E. O. Wollan, Ralph W. G. Wyckoff, Imaoka Yoshio, Suga Yosuke, and Rolland M. Zabel.

The regular scientific session consisted of forty-two papers, five of which—Nos. 1, 16, 17, 21, 38—were read by title. The abstracts of these papers are given on the following pages. An AUTHOR INDEX will be found at the end.

W. L. SEVERINGHAUS, *Secretary*

ABSTRACTS

1. Thermal expansion of "Carboloy." PETER HIDNERT, *Bureau of Standards.* Measurements have been made on the linear thermal expansion of two samples of "Carboloy" (a new tool material) purchased several months ago from Carboloy Company, Inc., 350 Madison Ave., New York City. An interferometer was used in the determinations at various temperatures between 20° and 400°C. The following results were obtained.

Sample	Heating	Average Coefficients of Expansion per Degree Centigrade				
		20 to 60°C $\times 10^{-6}$	20 to 100°C $\times 10^{-6}$	20 to 200°C $\times 10^{-6}$	20 to 300°C $\times 10^{-6}$	20 to 400°C $\times 10^{-6}$
1374 I	First	5.2	5.3	5.5	5.6	5.9
	Second	5.1	5.2	5.6	5.7	6.0
1375 I	First	5.0	5.2	5.5	5.8	6.0
	Second	4.9	5.2	5.5	5.8	6.0

The coefficients of expansion of "Carboloy" are larger than the corresponding coefficients of tungsten. For the range from 20° to 400°C, the average coefficient of expansion of the two samples of "Carboloy" is approximately 30 percent greater than the coefficient of expansion of tungsten.

2. Young's modulus determined with small stresses. DAROL K. FROMAN, *University of Chicago.* (*Introduced by A. J. Dempster.*)—An interferometer method, similar to that used by E. G. Grüneisen (Ann. d. Physik **22**, 801, (1907)), was used to determine the extensions of metallic rods under small stresses. The applied stresses ranged in value from less than 1 kg/cm² to the smallest usually used in commercial testing, about 300 kg/cm². For the substances examined, Young's Modulus was found to increase very rapidly as the stress increased from zero, to reach a maximum at a comparatively small stress, and then to decrease almost exponentially to the ordinary value. The maximum elasticity was found to be from 10 to 30

percent higher than that at large stresses. The annealing of the rods is probably connected with this divergence from Hooke's Law with small stresses, as slight differences were found on reannealing some of the rods.

3. The construction of a master clock with light controlled contacts. J. V. HOFFACKER, *Purdue University.* (*Introduced by K. Lark-Horovitz.*)—Mercury contacts for controlling circuits periodically by means of pendulums, because of their unreliability and their effect on the period of the pendulum, have been replaced by photoelectric cells influenced by beams of light interrupted periodically by the swinging pendulums. But since selenium cells are equally sensitive to light when operating with direct or alternating current they can be used with a specially constructed relay employing alternating current from lighting mains as the only source necessary. Low resistance selenium cells transformer coupled and high resistance cells as grid leaks in triodes have been used successfully. The relayed current rectified by a dry rectifier is used to keep the pendulum itself going so that no clockwork is necessary to operate repeater clocks.

4. The Nernst heat theorem. HERBERT J. BRENNEN, *Northwestern University.* The Gibbs-Helmholtz equation requires that the limit of $(\partial U/\partial T)=0$, as T approaches zero. Nernst makes the further assumption that the limit of $(\partial A/\partial T)=0$, as T approaches zero. On putting: $U=U_0-bT^2-2cT^3-$etc., integrating the Gibbs-Helmholtz equation and using Nernst's assumption, one finds: $A=U_0+bT^2+cT^3+$etc. Whence, $Q=A-U=2bT^2+3cT^3+$etc.; where A, Q, U and T have their usual significance. Hence, for small values of T, as a first approximation: $(\partial \log Q/\partial \log T)$ is equal to two, which is double that demanded by the Carnot heat theorem. In order to account for this discrepancy, it is suggested that: (1) since U is a function of the volume as well as the temperature, both U and T be regarded as independent variables and A, a dependent variable; (2) the Gibbs-Helmholtz equation be generalised to: $A-U=T(\partial A/\partial T)+KU(\partial A/\partial U)$ where K is a constant. This equation becomes identical with that of Gibbs and Helmholtz when $U=0$ or when A is independent of U.

5. Porous plug measurements with air. J. R. ROEBUCK, *University of Wisconsin.*—In an earlier article (Proc. Amer. Acad. **60**, 537, (1925)) I described apparatus and methods used for measuring the Joule-Thomson coefficient over 25 to 280°C and 1 to 215 atm. The present work extends the data down to −150°C. The measurements give isenthalpic curves in a pressure-temperature field. The derivative $(dT/dp)_h=\mu=$Joule-Thomson coefficient has been plotted as a function of p and T over the whole field. The original curves were used to spread C_p at 1 atm. over the 215 atm. range. With the aid of data on (pv) for air taken from the literature, the free-expansion (Joule) coefficient $(dT/dp)_u=\eta$ has been calculated over −100° to +200°C and 1 to 100 atm. These again give the elastic coefficient $1/v(dv/dp)_t=\gamma$ and $(du/dv)_t=\lambda$ over this field. λ can be used to calculate the correction to the constant volume air temperature scale, which is being done. This completes the work with air, and the apparatus is being rebuilt into a closed system to measure pure gases of which the first is to be helium.

6. The function of the base metal in oxide coated filaments. E. F. LOWRY, *Westinghouse Elec. & Mfg. Co., East Pittsburgh.*—Measurements on a number of UX-281 Radiotrons with oxide coated platinum-iridium filaments and others having oxide coated "Konel" filaments show that the base or core metal plays an important part in the behavior of such filaments. Konel, an alloy of nickel, cobalt, iron and titanium, has a much higher thermal emissivity than platinum and therefore, when operated at 4 watts per cm², reaches a temperature about 150°C lower than that reached by oxide coated platinum with the same energy input. Nevertheless, oxide coated Konel filaments give slightly higher emissions than oxide coated platinum filaments under like conditions of input energy. This anomalous behavior requires a modification of the present theory of oxide emission. This requirement is met by assuming that the source of the electron emission is a layer of metallic barium in contact with the base metal and that the electrons diffuse through the pores in the oxide coating which is a rather good non-conductor. This hypothesis serves as a satisfactory basis of explanation for the varied and somewhat confusing phenomena of oxide emission.

7. Photoelectric behavior of solid and liquid mercury. DUANE ROLLER, *University of Oklahoma.*—With monochromatic light, the photoelectric threshold for solid mercury, freshly distilled in vacuum, was found at 2750 ± 25A for all temperatures between -190°C and the melting point. The threshold for liquid mercury at room temperature was at 2735 ± 10A, confirming the value established earlier by Kazda and by Hales. The emission for monochromatic light was independent of the temperature between -190° and -40°C. There was no indication of a change in the crystal structure of mercury in this region of temperatures. The emission for the solid phase was always somewhat higher than that for the liquid at room temperature, possibly due in part to a change in the optical absorptivity of the mercury surface with change in phase. A study of the optical absorptivity of solid mercury is in progress. Between -39° and 0°C the emission was about 75 percent of that at room temperature but showed hysteresis with successive warming and cooling of the mercury. Thus a further study of liquid mercury between melting and room temperatures is needed. Most of this work was done at the California Institute of Technology.

8. Spatial distribution of photoelectrons. S. SZCZENIOWSKI, (*International Education Board Fellow*) *University of Chicago.*—The perturbation of a hydrogen-like atom by a plane polarized electromagnetic wave is considered on the basis of Dirac's equations, and perturbed wave-functions are obtained. These functions lead by a method similar to that used by Sommerfeld in his "Wellenmechanisches Ergänzungsband," to a formula for the spatial distribution of the photoelectrons, but differing from his in the first approximation, by a factor equal to 5/9. This factor follows from a consideration of the normalization factors for the spherical harmonics, which were not introduced by Sommerfeld. A second approximation has also been obtained showing the influence of electron spin. This formula differs from that obtained by Carrelli (Zeits. f. Physik **56,** 694, (1929)) in that the spin and some other terms not considered by Carrelli appear.

9. Electron velocities in an electrodeless discharge. CHARLES J. BRASEFIELD, *University of Michigan.*—A high frequency discharge in hydrogen was obtained by applying high frequency voltages to the movable external electrodes of a cylindrical discharge tube. By observing the change in the ratio of the densities of certain singlet and triplet lines of the secondary spectrum (see Phys. Rev. **34,** 437 (1929)), the mean electronic velocity in the discharge was studied as a function of (1) the frequency of oscillation, (2) voltage between electrodes, (3) distance between electrodes and (4) gas pressure. Observations were made at frequencies of oscillation corresponding to the wave-lengths 15, 25, 50, 100 and 200 meters. For example, at 0.03 mm pressure with 1400 volts applied to the electrodes, the electronic velocity increases from 23.7 volts at 25 meters to 25.8 volts at 200 meters. At 25 meters and 0.03 mm pressure, the electron velocity increases from 20.8 volts to 23.7 volts as the voltage between electrodes is increased from 500 volts to 1400 volts. Finally, at 25 meters with 1000 volts between electrodes, the electron velocity increases from 22.7 volts to 24.7 volts as the pressure is reduced from 0.06 mm to 0.01 mm. It appears that conditions in the electrodeless discharge should be quite similar to those in the positive column of an ordinary Geissler tube discharge. This probably explains why such small changes in electronic velocity were observed.

10. Motion of electrons in carbon monoxide. H. B. WAHLIN, *University of Wisconsin.*—In a paper which appeared in an earlier issue of the Physical Review [**21,** 517 (1923)] it was shown that the mobility of electrons in CO obey the equation $U = A/[B+V]^{1/2}$ with a high degree of accuracy. Shortly after the appearance of this paper K. T. Compton showed that the equation for the mobility should be of the form $U = A/[1+(1+BV^2)^{1/2}]^{1/2}$. Application of this equation to the data presented earlier shows that for low fields the Compton equation holds within the limits of experimental error. At values of X/P above 0.4 volts/cm/mm pressure a systematic deviation from this equation appears due probably to a decrease in the electronic free path with increasing electron velocity. The electron free path in thermal equilibrium with the gas and at a pressure of 1 mm is found to be 0.069 cm.

11. Slow caesium ions in hydrogen and helium. J. S. THOMPSON, *University of Chicago*, (*Introduced by A. J. Dempster.*)—The motion of positive caesium ions in hydrogen and helium has been examined for ion velocities ranging from 3 to 600 volts. Three different experimental arrangements were used in which the ions traversed a known gas path and in which any weakening of the bundle could be observed. No absorption of 10 to 600 volt ions was observed for gas pressures up to 0.030 mm of Hg. At the highest pressure the ions make 20 collisions without deflections from their original directions. Below 10 volts and for pressures above 0.010 mm a definite weakening of the bundle sets in and increases rapidly with the pressure. In all cases studied the ions were retarded, and the velocity distribution produced has been measured. The final velocities show an approximate probability distribution about a mean retardation. This distribution becomes more nearly that of the error curve for smaller velocities and higher pressures. The large absorption of the caesium ions observed by Ramsauer is accounted for on the basis of this retardation. Lithium ions in helium show considerable scattering which decreases as the velocity is increased and rises rapidly as the velocity is reduced below 50 volts.

12. Ionization efficiency of electrons in potassium vapor. J. KUNZ AND A. HUMMEL, *University of Illinois.*—Using a direct method in which a beam of electrons is projected into a field-free chamber, the number (N) of positive ions formed per electron per centimeter path per unit pressure has been measured and plotted against the energy of the primary electron. Scattering of the primary beam was prevented by means of a magnetic field of 350 to 400 gauss parallel to the beam. A small transverse electric field was employed to drive the positive ions to the collecting plate. Two other plates served to make this field uniform in the region from which the ions were collected. For potassium vapor N was found to have three maxima occurring at 40, 81, and 122 volts accelerating potential. The second and third maxima are respectively 18 percent and 11 percent greater than the first. N is approximately 20 times the value of N for argon. The curve for argon has a maximum value for N of 0.108 appearing at 88 volts which compares with the maximum 0.113, at approximately 125 volts, observed by Compton and Van Voorhis.

13. A study of the ions produced in mercury vapor by electron impact. WALKER BLEAKNEY, *University of Minnesota.*—In a recent paper (Phys. Rev. **34**, 157 (1929)) a method was proposed for analyzing the primary results of ionization by electron impact. The method has been applied to a quantitative study of the five mercury ions Hg^{+}, Hg^{2+}, Hg^{3+}, Hg^{4+} and Hg^{5+}. The results show that the fraction of the current carried by the Hg^{+} ion falls rapidly from 100 percent at electron velocities between 10.4 and 30 volts to about 70 percent at 100 volts, and then approaches a nearly constant value of about 60 percent for increasing electron speeds. At 300 volts the fractions of the total positive ion current carried by the five ions, in order, are 59, 26, 11, 3.5, and 0.5 percent respectively. The results have been reduced to number of ions per electron per cm path per mm pressure at 0°C as a function of the electron velocity. These data show a distinct maximum of magnitude about 21 for the Hg^{+} ion in the neighborhood of 50 volts while the value at 300 volts has dropped to half as much. Maxima also appear for Hg^{2+} and Hg^{3+} at 115 and 210 volts respectively.

14. Absorption of lithium ions in mercury vapor. I. W. COX, *University of Chicago.* (*Introduced by A. J. Dempster.*)—The absorption of 25 to 300 volt lithium ions in passing through mercury vapor at various pressures up to 48×10^{-4} mm was observed by two different methods. In the first method the ions described a semicircular path in a magnetic field and the decrease as the pressure was increased was observed. In the second method the ions, after this magnetic analysis, described a straight path to a collecting chamber and the decrease in the number entering the circular aperture of the collecting chamber was observed as the pressure was increased. A consistent difference was found in the absorption coefficients given by the two methods. It was also altered by a change in the aperture of the collecting chamber in method 2. This indicates that the collisions with the mercury atoms are not elastic, but that a large fraction of the deflections are through small angles. Ionic diameters deduced from the absorption depend on the apertures of the apparatus used. The ions collected are not slowed

up appreciably, and there is a dependence of the absorption observed with any particular aperture on the velocity of the ions.

15. The reflection of lithium ions from metal surfaces. R. B. SAWYER, *University of Chicago.* (*Introduced by A. J. Dempster.*)—Experiments have been performed on the reflection of lithium ions from reflectors of platinum foil and of nickel crystals deposited on tungsten foil (Rupp, Ann. d. Physik [5], **1**, 801 (1929)). Movable ground joints in the tube were entirely eliminated. Readings were taken with both cold and hot reflectors. Spodumene was used as a source of ions and reflection was studied in the meridian plane only. Superposed on a diffuse scattering of ions were two reflected beams. One was reflected nearly specularly, as found by Read (Phys. Rev. **31**, 155 (1928)) and Gurney (Phys. Rev. **32**, 467 (1928)), the angle of maximum reflection, however, being independent of accelerating potential. The other beam appeared only at voltages above 200 or 250 and was composed of ions most of which had retained 80 percent or more of their original energy. This beam was found between the incident beam and the normal to the surface, at angles independent of the accelerating potential up to 700 volts. This independence of angle on voltage forbids diffraction interpretations. A tentative explanation consists in supposing specular reflection from the (110) planes of the nickel cyrstals, but the agreement is not entirely satisfactory.

16. Secondary emission of nickel under positive ion bombardment in the positive column in neon. W. UYTERHOEVEN AND M. C. HARRINGTON, *Princeton University.*—An attempt is made to measure the secondary emission under positive ion bombardment of metal collectors in the positive column under conditions as near as possible to those in the cathode fall. A combination of a fixed collector and a movable one opposite the first, was used. The movable one was given a negative potential and the ion current to it compensated; then the potential of the fixed electrode was varied and the corresponding change in current to each measured. The results obtained so far show that for an accelerating potential of about -150v, the secondary emission can reach 50 p.c. of the total current collected on a negatively charged electrode. (Proc. Nat. Ac. Sc. **15**, 32 (1929)). The electron mean free path seems to depend markedly on the degree of ionization of the gas, the measured values being less than the gas kinetic values (e.g. 50 p.c.). A large fraction of the electron emission from the metal is apparently due to the impact of metastable atoms on the collector. (Oliphant, Proc. Roy. Soc. **A124**, 228 (1929)), but for higher accelerating potentials of the positive ions their effect becomes more and more important (Penning, Physica, **8**, 13 (1928)).

17. Zeeman effect in λ5211 MgH band. G. M. ALMY, F. H. CRAWFORD AND E. L. HILL, (*National Research Fellow*), *Harvard University.*—The Zeeman effect for molecules lying between Hund's cases (a) and (b) has been treated theoretically by the quantum mechanics, and the results applied to the MgH band at λ5211. For states near case (a) the theory predicts the usual splitting into $(2J+1)$ magnetic substates. When the magnetic separations are comparable with the doublet separations (very high fields or small doublet intervals) a Paschen-Back effect sets in corresponding to uncoupling of the electronic spin and the rest of the molecule with a degeneration of the term system into that of a symmetrical top superposed on that due to practically free spin. In a $^2\Sigma$ state (neglecting rho-type doubling) this degeneration is sensibly complete at all fields. The theory is verified quantitatively in the λ5211 MgH band. In the earlier lines the size of the fine structure patterns agrees numerically with calculations. In the higher lines the Paschen-Back effect causes a filling in of the normal doublet interval with an unresolved band in addition to the appearance of outer wings which move out and become fainter with field. Pattern widths, separation of components, and line displacements, where observable, have been measured from plates taken at fields between 5000 and 28000 gauss. No detailed intensity calculations have been made.

18. A magneto-optic method of chemical analysis. FRED ALLISON AND EDGAR J. MURPHY, *Alabama Polytechnic Institute.*—This is a refinement of a method previously reported by one of us (Allison, Phys. Rev. **30**, 66 (1927) and **31**, 313(A) (1928)). Each chemical compound produces a minimum of light at a point characteristic of the compound. The surprising result

has been found that this characteristic minimum does not disappear until the concentration has been reduced to less than one part in 10^{10}. The method thus affords a very sensitive and rapid means of chemical analysis. A large number of such analyses has been made. The presence of compounds, instead of elements, is detected. Each inorganic compound is characterized by either a single minimum or two or more close minima. The number of these minima, with few exceptions, is the same as the number of known isotopes of the metallic element of the compound. The investigations have been confined to a number of organic liquids and an extensive series of nitrates, chlorides, sulphates and hydroxides in solution. The positions of the minima are some inverse function of the chemical equivalent of the metallic element of the inorganic compounds. The effect is no doubt a time effect, but a complete interpretation must await further investigations, which are in progress.

19. The absorption spectrum characteristic of vitamin A. JAY W. WOODROW AND H. L. CUNNINGHAM, *Iowa State College.*—The absorption spectra of substances containing vitamin A were obtained in the region from 290 to 350 mμ by means of a sensitive photoelectric spectrophotometer. Fresh cod-liver oil and spinach juice gave prominent absorption bands with maxima at 310 and 326 mμ with minor bands at 320, 330 and 337 mμ. When the oils were extracted with ether, the bands were shifted toward the shorter wave-lengths by 3 mμ but their relative intensities remained the same. These bands were obtained with cod-liver oil, spinach juice, egg yolk and butter, all of which are known to be rich in vitamin A. Peanut oil which is rich in vitamin D but contains no vitamin A, gave the characteristic vitamin D bands at 270, 280 and 290 mμ but gave no indication of the bands in the neighborhood of 326 mμ. Bubbling air through the cod-liver oil at a temperature of 90°C for an hour or exposing it to the ultra-violet light from a quartz mercury arc for 20 min., either of which will destroy most of the vitamin A, caused the disappearance of the absorption bands at 310, 320, 326 and 330 mμ.

20. A new absorption band of atmospheric oxygen and the vibrational frequency of the normal molecule. HAROLD D. BABCOCK, *Mount Wilson Observatory.*—Four possible absorption bands in the "atmospheric" system of oxygen have been sought with air paths of 40 to 70 kilometers, (0, 1), (2, 1), (2, 2), (1, 1). The last has been discovered; the others are not yet established. The intensity of (1, 1) is roughly 1/2500 that of (0, 0). Over 30 lines are identified and 26 are accurately measured. Wave-number differences are taken from these to corresponding lines in (0, 0), (1, 0), (2, 0) and (3, 0). Eliminating the rotational effect and using the known spacing of the vibrational levels in excited O_2, these combinations give 1556.31 ± 0.05 cm^{-1} as the most probable value of the vibrational frequency of the normal molecule having 1 unit of vibrational energy. Results from *P* branches are more concordant than from *R* branches, which show a slight linear dependence on the upper vibrational state. The new value is compared with the Raman displacement, and its usefulness is discussed in other relations such as, calculation of isotopic displacement and of heat of dissociation. The data also help to establish a test for the consistency of solar standards of wave-length.

21. On the active nitrogen glow. RICHARD RUEDY, *Toronto.*—With strong afterglows in N_2 the 3 prominent bands can be seen for several seconds; such a persistence is longer than the time necessary for the recombination of N atoms (the formation of H_2 being taken as a basis of comparison) and considerably longer than the life of metastable systems. However, the potential energy curve for the initial state of the afterglow bands shows that, although emission of light takes place when during their oscillations the atoms have reached their greatest elongation, dissociation is likely to occur at the inner turning point, particularly for the smaller heats of dissociation which have found favor since it was shown that no Xe lines could be obtained in the afterglow, (Trans. R. Soc. Can. **22,** 303 (1928)). This dissociation process provides for the afterglow the necessary number of atoms, and eventually for metastable atoms. The real excitation potential of level *A* seems to be below 7 volts. In a 1 to 2 *l* bulb an initial intensity of the glow, corresponding to about one candle, can be obtained at a few mm Hg, and a total intensity of a few candles. This corresponds to 10^{17} emission processes initially, or to 10^{14} radiating molecules per cm^3 (10^{-3} mm Hg), an insufficient amount for ordinary absorption measurements.

22. The excitation of certain nitrogen bands by positive ion impact. H. D. SMYTH AND E. G. F. ARNOTT, *Princeton University.*—In the sources of light usually used for the study of band spectra excitation is chiefly by electron impact. It is now generally agreed that an electron impact does not alter the rotational nor vibrational momentum of a molecule. However, it might be expected that in excitation by positive ion impact both the vibrational and rotational momentum might be altered. We have, therefore, undertaken the study of the intensities of band spectra excited in nitrogen by the impact of mercury ions. Mercury canal rays pass through the cathode of a discharge tube into an atmosphere of nitrogen. The feeble light excited is found to consist almost exclusively of the negative nitrogen bands. In the two bands (λ4278 and λ3914) which have been photographed with a small grating, the lines corresponding to the lowest rotational states are definitely weaker than in comparison photographs taken with an electrodeless discharge. In fact the first two lines of the *R*-branch and the first line (perhaps the first two) of the *P*-branch are entirely missing. Theoretically one might expect one more line of the *P*-branch than of the *R*-branch to be missing. The investigation is still in a very preliminary stage.

23. The spectrum of singly ionized indium. R. J. LANG, *University of Alberta* AND R. A. SAWYER, *University of Michigan.*—The indium spectrum has been excited in a hollow cathode discharge in helium, using the same technic as in the authors' previous work with gallium. The spectrum has been photographed throughout the entire photographic region. The first spark spectrum is a two electron spectrum with singlet and triplet terms of which the chief combinations have been identified. Enough higher terms have been found to permit the calculation of approximate term values. The deepest term, $(5s^2)^1S$, is placed at 152350 cm^{-1} corresponding to an ionization potential of 18.81 volts.

24. Intensity measurements in neon spectrum. H. N. SWENSON, *University of Illinois.*—The Ornstein method of photographic photography has been applied to a study of the neon discharge. Special emphasis was placed upon elimination of errors in the optical system and in the development of plates. Density screens were prepared by sputtering platinum films of various densities on quartz plates. This screen was placed in an optical system similar to that of Ornstein and vibrated electrically to eliminate possible errors due to non-uniformity. Development was carried out at constant temperature and with forced circulation of developer around the plate. Intensity ratios were obtained for 19 lines in the region from 5800A to 6700A. The discharge was excited by a 10,000 volt transformer, the pressure being 2 mm. The intensity ratios for multiplets which are transitions from the same upper level, are not in agreement with the values of Dorgelo or those predicted by the Ornstein-Burger intensity rules, but show marked agreement with values recently published by Ende using electron impact excitation.

25. Intensity relations in some of the stronger multiplets of chromium I and chromium II. CEDRIC E. HESTHAL, *Ohio State University.*—The relative intensities of thirteen multiplets in the spectrum of chromium I and of five multiplets in the spectrum of chromium II have been determined by photographic photometry. The method used was that described by G. R. Harrison in the Journal of the Optical Society (**17**, 389 (1928); **18**, 287 (1929)). Numerous violations of the intensity formulas which have been derived by H. N. Russell, R. de L. Kronig and others are found. In some multiplets all the lines appear anomalous while in other multiplets only a fraction of the lines are abnormal. In general, the violations are more numerous than those observed by Harrison in titanium and fewer than those observed in iron and nickel by Ornstein, showing that perturbations increase with atomic number among the elements of the iron group. The intensities of multiplets forming two triads have also been determined and the equivalent excitation temperatures for these calculated. For one of these triads the method fails showing that this triad does not obey the formulas of R. de L. Kronig while for the other, temperatures between 2800°K and 4800°K were observed for different exposures. Data have been obtained to show that the equivalent excitation temperature is not the same for multiplets having final states in different regions of the atom.

26. Relations between hyperfine structure separations. S. GOUDSMIT AND R. F. BACHER, *University of Michigan.*—The quantum mechanics conception of a spinning electron in an s-state makes it probable that its interaction energy with a nuclear moment i is simply proportional to the average of $is\cos(i\cdot s)$. In some cases where the hyperfine structure is mainly caused by an s-electron one can evaluate this cosine. This gives relations between the hyperfine structures of different levels which agree well with observations on Tl II (McLennan).

The large hyperfine structures in Tl II are due to the presence of the deeply penetrating single $6s$-electron, those of Tl I are much smaller ($6s^2$). In Tl III only the normal state $6s$ will show a very large hyperfine structure which must be about 8 cm^{-1}. In more complicated cases one can only tell that the interaction energy will be proportional to $ij\cos(i\cdot j)$ which causes the interval rule to be valid for hyperfine structure.

27. Relativity transformation of an oscillation into a traveling wave, and de Broglie's postulate in terms of velocity angle. VLADIMIR KARAPETOFF, *Cornell University.*—The author has previously described a method of representation of space-time relationships in restricted relativity, by means of oblique coordinates (J.O.S.A. and R.S.I. **13**, 155 (1926)). The theory has been applied to the following problem: Two observers, S and S', are moving at a relative velocity q. The S' observer has in his system a set of pointers oscillating in synchronism and in phase with one another. It is required to describe the motion as seen by the observer S. By drawing two sine waves in the Lorentzian plane, it is shown graphically that for the S observer the pointers do not swing in synchronism, but form a traveling wave whose velocity of propagation, u, is connected with q by the familiar relationship $uq=c^2$, where c is the velocity of light.

Introducing the so-called velocity angle, α, determined by the relationship $\sin\alpha=q/c$, various other properties of the traveling wave, as seen by S, have been deduced, such as the apparent frequency at a point in space, the apparent amplitude and its velocity of propagation, the Fitzgerald contraction of the oscillating system, the slowing down of the frequency of oscillation, the group velocity of "super-light" waves, and de Broglie's quantum principle. The article appeared in the Journal of the Optical Society of America for November, 1929.

28. The significance of the Michelson-Morley-Miller experiments in relation to the restricted theory of relativity. W. F. G. SWANN, *Bartol Research Foundation.*—While aether drift experiments originally suggested the line of thought which leads to the formulation of the restricted theory of relativity, it would seem that the fundamental significance of that theory does not depend primarily upon these experiments. The most logical origin of the transformation of the restricted theory is to be found as a special case of the general theory, and the purpose of the present paper is to show how, with this in view, the fundamental working content of the restricted theory, the invariance of laws under the Lorentzian transformation, is something which has no fundamental relation to the question of whether the aether drift experiments do or do not give a positive result.

29. Electron distribution in magnesium oxide. ERNEST O. WOLLAN, *University of Chicago.* (*Introduced by A. H. Compton.*)—The intensity of x-rays reflected from powdered crystals of magnesium oxide were measured for all lines out to $\theta=45°$. The values of the structure factor, F, were calculated and plotted against $\sin\theta$. Using the values of F from this curve as coefficients in the Fourier Series given by Compton ("X-Rays and Electrons") the radial electron distribution for the atoms of magnesium and oxygen was determined. The electron distribution curves for these atoms are very similar to the curves by Havighurst (Phys. Rev. **29**, 1 (1927)) for NaCl and NaF. However, the data indicate that the number of electrons associated with magnesium and oxygen is more nearly that of the neutral atoms than that of the ions, whereas Havighurst concludes that the lattice points are occupied by ions. A recalculation of some of Havighurst's data brings results which are in closer agreement with those of the author.

30. The efficiency of x-ray fluorescence. A. H. COMPTON, *University of Chicago.*—A review of the published data describing the intensity of fluorescent x-rays shows that the various observers agree that the number of quanta of fluorescent x-rays emitted by a radiator is con-

siderably less than the number of quanta which it absorbs from the primary beam. The values of the efficiency of fluorescence that appear in the literature are for the most part, however, found not to be quantitatively reliable. New experiments give values of the "fluorescence yield," or ratio of the number of fluorescent K quanta to the number of photoelectrons ejected from the K shell, of 0.68 for a molybdenum radiator, 0.56 for bromine, 0.54 for selenium, and 0.37 for nickel. The values seem to be independent of the wave-length of the exciting rays. These measurements agree within experimental error with Auger's values of the fluorescence yield, based on his count of the frequency of occurrence of the compound photoelectric effect, and thus indicate that it is this effect which makes the fluorescence yield less than unity. Knowledge of the fluorescence yield gives an expression for calculating the relative intensity of two x-ray beams of different wave-length, in terms of the ionization currents obtained, and other factors.

31. Efficiency of production of continuous spectrum x-rays. WARREN W. NICHOLAS, *Bureau of Standards.*—There is a large discrepancy between the efficiency estimated by Kulenkampff (Handbuch der Physik vol. 23), who found $k=8\pm2\times10^{-10}$ in the formula, *efficiency* $=kZV$, where Z is the atomic number of the anticathode material and V is the potential across the tube in volts and the more recent experimental determination by Rump, who found k to be about 15×10^{-10}. This discrepancy makes desirable a closer consideration of some of the secondary processes (reflection of cathode rays from anticathode, etc.) occurring in both gas filled and hot cathode x-ray tubes, as well as a further examination of corrections for absorption (including absorption in the anticathode) and for asymmetric spatial distribution of x-ray energy. A correction of Rump's data on this basis leads to a value of k about 10×10^{-10}. Some estimates of actual x-ray energy, both continuous and characteristic, obtained outside a tube are obtained incidentally.

32. Absolute measurement of certain x-ray wave lengths. J. M. CORK, *University of Michigan.*—An x-ray vacuum spectrograph employing a plane glass grating 30,000 lines per inch and having a distance between grating and photographic plate of one meter has been used to obtain the absolute wave-length value of the L-series emission lines for elements molybdenum (42) to antimony (51). In addition many other lines are present due to extraneous sources in the x-ray tube. These wave lengths have been previously accurately measured by many observers employing the crystal method. A comparison of the two sets of values is made bearing on the question regarding the Avogadro number and electronic charge. The results obtained for the wave-lengths of the two molybdenum lines $L\alpha$ and $L\beta_1$, are respectively 5.3943 and 5.1658 A.U., indicating for e the value 4.821×10^{-10} e.s.u.

33. The index of refraction and absorption coefficient of gold for the Kα line of carbon. ELMER DERSHEM, *University of Chicago.*—An experimental curve showing the intensity of reflected radiation plotted against glancing angle of incidence was obtained for a sputtered gold surface and the $K\alpha$ line of carbon ($\lambda=44.6$A) by the use of methods and apparatus previously described (Phys. Rev. **34**, 1015 (1929)). The absorption coefficient (μ) of gold leaf for this wave-length was measured and a value of the extinction coefficient (κ) determined from the relation $\kappa=\mu\lambda/4\pi$. The experimental value being $\kappa=0.0086$. A computation by the use of the Drude-Lorentz dispersion formula gives $1-n=\delta=0.009$ for the case of gold and this wave-length. These values of κ and δ were substituted in a modified form of the Fresnel reflection equations and a theoretical curve relating reflected intensity and glancing angle was thus obtained. To secure perfect agreement with the experimental curve either κ or δ or both must have smaller values. Hence curves are also computed with various pairs of arbitrarily assigned values of κ and δ which show the effect of changes in the values of these constants upon the theoretical curve.

34. Diffraction of x-rays in liquids and the effect of temperature. E. W. SKINNER, *University of Iowa.*—Fourteen liquids have been examined for x-ray scattering both at room temperature and close to their boiling points. Results for principal maxima are as follows: 1. Change in intensity. a. Heptyllic acid, cyclohexane, benzene, octane, lauryl alcohol, and 2–7 dimeth-

yloctane show a decrease in intensity with increase in temperature. b. Mesitylene, di-n-propyl carbinol, tertiary butyl alcohol, 4 hydroxy 1–3 dimethylbenzene, 2 hydroxy 1–3 dimethylbenzene, 2–2–4 trimethylpentane, phenol, and napthalene show an increase in intensity with increase in temperature. 2. An increase in molecular dimensions at higher temperatures was found, and, in general, the change is in agreement with the expected change in density due to expansion. 3. Change in peak width. The large peak common to all liquids thus far examined in this laboratory, appears to be wider at higher temperatures in all cases which is in agreement with existing theories of temperature effect in crystal scattering. All results are shown to be in agreement with the theory of the cybotactic condition except that an additional effect is needed to account for (1b).

35. Polarization of x-rays from thin aluminium anti-cathodes. BALEBAIL DASANNACHARYA, *University of Chicago.* (*Introduced by A. H. Compton.*)—An electron-beam 5 mm in diameter falls on thin aluminum foils of thickness varying from 6–250.10^{-5} cm, mounted on a cylindrical frame-work attached to a glass tap and regulated from outside. A graphite plate on an ionization spectrometer served to measure the polarization. The voltages varied from 27–56 KV. For a given voltage, polarization increases slowly at first with diminution of thickness but rises exponentially for thicknesses smaller than 2.5.10^{-4} cm. For different voltages the form of the curves remains the same, but the value of the polarization slightly diminishes with increase of voltage. The maximum polarization obtained was 47.5 percent. It looks likely that for a thickness of about 5.10^{-6} cm the polarization would be complete.

36. A relation between the Compton effect and the diffraction by electrons. JAKOB KUNZ, *University of Illinois.*—In the Compton effect a quantum of radiation of momentum $h\nu/c$ is transformed into the momentum of an electron mv and into a weaker quantum of radiation of momentum $h\nu'/c$. If we assume that the reversed process also is possible and that an electron strikes a quantum head on, then we obtain: $mv = h\nu/c = h/\lambda$, or $\lambda = h/mv$, which is the relation given by wave mechanics for the diffraction of electrons.

37. Paschen-Back effect of hyperfine structure. S. GOUDSMIT AND R. F. BACHER, *University of Michigan.*—By replacing the quantum vectors (s, l, j) and the magnetic moments (sg_s, lg_l, jg_j), of the ordinary multiplet theory by those of the hyperfine structure theory $(i, j, f; ig_i, jg_j, fg_f)$, it is possible to adapt the work of Heisenberg, Jordan and Darwin on Zeeman effect and intensities in any field strength, to the study of the Zeeman effect of hyperfine structure. The thallium line $(6p^2P_{1/2} - 7s^2S_{1/2})\lambda 3776$ is an example of incomplete Paschen-Back effect which can be treated quantitatively with the above method. The calculated splitting up of this line in a field of 43350 gauss is in cm^{-1}. −3.00, −2.52, (−1.43), −(1.20), (+1.28), (+1.36), +2.45, +3.08. Measurements by Professor E. Back and Dr. J. Wulff at Tuebingen give −3.02, −2.54, (−1.42), (−1.22), (+1.35 strong), +2.43, +3.10. Without hyperfine structure the Zeeman effect would have been (±1.36), ±2.71.

38. Rectifier characteristics and detection diagrams. RICHARD RUEDY, *Toronto.*—The average current I_m obtained per cycle when, in addition to the constant voltage E, the potential $E_0 \sin \omega t$ is applied to a rectifier possessing the characteristic curve $I = f(E)$, has been calculated and compared with experiment for different $f(E)$. The curve $I = c\epsilon \exp [E/e_c]$ giving at open circuit a voltage independent of E applies to all types of vacuum tubes when the A.C. voltage does not exceed a few tenths of a volt, or 0.5 volts in the case of oxide-coated emitters. The curve $I = I/E$ gives $I_m = I/(E^2 - E_0^2)^{1/2}$, and applies to certain types of glow and arc discharges in which an a.c. e.m.f. is superimposed upon d.c. Parabolic curves, for which the increase in I is independent of E, represent the actual current I_m better than the theoretical curves $I = CE^{3/2}$.

39. A new equation of state. HERBERT J. BRENNEN, *Northwestern University.*—Dieterici (Ann. d. Physik **66**, 826 (1898)) put forward the equation of state: $P(V-b) = RT \exp(-A/RT)$ where P, V and T are the pressure, volume and temperature, respectively, and A, b and R are parameters. However, limit (PV/T), as V becomes infinite, is equal to R and has the same value for one mole of all substances. Hence, we may replace RT by a new variable E and

Dieterici's equation becomes a two parameter equation. Since, a straight line intersects this equation in three real finite points at temperatures below the critical temperature, mathematical theory demands, in general, three parameters which makes Dieterici's equation, in general, mathematically absurd. Accordingly, I propose the new equation: $P(V-b)=RT \exp[-A(V-b)/RTV^n]$ which, for large values of V becomes identical with the equation (Proc. Nat. Acad. Sci. **15**, 11–18, Jan. (1929)) already proposed by me, and where n is the third or missing parameter. This new equation predicts that the Law of Corresponding States is true only for substances having the same values of the critical ratio, RT_c/P_cV_c.

40. On the origin of the line absorption spectra of the rare earths. OTTO LAPORTE, *University of Michigan.*—In the rare earth group of elements the configuration $4f^n$, $4f^{n-1}5d$, $4f^{n-1}6s$ will compete in the formation of the lowest terms. For neutral atoms or ions of low order, terms with $5d$ and $6s$ electrons will be most stable; for higher ionizations, terms due to $4f$ will be lowest, as is easily seen by comparing the slopes of the Moseley curves of the three configurations in question. Consequently, there will be intermediate stages of ionization, where the Moseley lines of the $4f^n$ and $4f^{n-1}5d$ terms cross, and spark spectra, for which the frequency of the allowed transition $4f^n-4f^{n-1}5d$ lies in the visible or at least at much longer wave-lengths than is usual for ions of (say) third or fourth order. The sharp absorption lines exhibited by rare earths in the liquid or crystal state are believed to be due to this transition. The fact that the absorption lines of gadolinium, recently measured by Freed and Spedding (Phys. Rev. **34**, 945, (1929)) lie farther towards the violet than those of any other rare earth may be understood in analogy to the group-theoretical ionization potentials as obtained by Peierls (Zeits. f. Physik **55**, 738, (1929)).

41. Further experiments on the disintegrative synthesis of oxygen of atomic weight 17 from nitrogen of atomic weight 14. WILLIAM D. HARKINS, *University of Chicago*, AND ARTHUR E. SCHUH, *Bell Telephone Laboratory.*—By the method of Harkins and Ryan (J. Am. Chem. Soc. **45**, 2095 (1923)) approximately 34,000 photographs of alpha ray tracks from thorium C and C' were taken as they appeared in a modified Wilson-Shimizu apparatus. Two disintegrative syntheses were given by 270,000 tracks of 8.6 cm and 145,000 tracks of 4.9 cm range in air. The gas used was nitrogen. It may be assumed that the alpha-particle attaches itself to the nitrogen nucleus, thus forming the nucleus of an atom of fluorine, which in less than a millionth of a second emits a fast hydrogen particle (proton) thus giving an oxygen nucleus of mass 17. By the use of the same general procedure Blackett (Proc. Roy. Soc. **A107**, 349 (1925)) obtained eight, and Harkins and Shadduck (Proc. Nat. Acad. Sci. **12**, 707 (1926)) obtained two such disintegrative syntheses. In this work 38 "collisions" of the alpha-particle were found in which the alpha-particle is deflected by more than 90°, while in the work of Harkins and Shadduck about 30 such collisions were found. If it is assumed that only such approximately direct impacts give a probability of a disintegrative-synthesis, then the possibility that the nitrogen thus transformed has an atomic weight of 15 seems negligible. A special search was made for the much more numerous short range hydrogen particles assumed by some workers to be emitted, but none of these were found. Thus far in this laboratory about 8 disintegrative syntheses per million long range alpha-particles, have been observed. Thus about eight protons per million long range alpha-particles were obtained in nitrogen, while Rutherford and Chadwick observed two with aluminum. However their scintillation method is not exactly comparable.

42. An isotope of nitrogen, atomic weight 15. S. M. NAUDÉ, *University of Chicago.* (*Introduced by Elmer Dershem.*)—(The abstract of this paper appeared as a Letter to the Editor, (Phys. Rev. **34**, 1498 (1929)). The following slight corrections should, however, be made in the calculated value of the wave-lengths of the isotope heads: Q_1 heads: 2155.263($N^{14}O^{17}$), 2155.753($N^{15}O^{16}$), 2156.744($N^{14}O^{18}$). P_1 heads: 2156.498($N^{14}O^{17}$), 2156.978($N^{15}O^{16}$), 2157.949 ($N^{15}O^{18}$). For the (0, 0) band the calculated shifts of the P_1 head are for $N^{14}O^{17}$, $N^{14}O^{18}$ and $N^{15}O^{16}$, -2.595 cm^{-1}, -4.952 cm^{-1} and -3.375 cm^{-1} respectively. This corresponds to the wave-lengths 2269.536A, 2269.659A and 2269.577A.

The third from the last paragraph of the letter should read as follows: "The effect on the (0, 0) band is very difficult to observe owing to its smallness. The wave-lengths of the displaced heads found are 2269.60($N^{15}O^{16}$) and 2269.70($N^{14}O^{18}$) which correspond within experimental error with the calculated shift. The displaced head due to the $N^{16}O^{17}$ molecule could not be observed."

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PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE STANFORD MEETING, DECEMBER 7, 1929

The 160th regular meeting of the American Physical Society was held in the main lecture room of the Physics Department of Stanford University, Stanford University, California, on Saturday, December 7, 1929. There were fifty members in attendance.

There was no business of importance transacted at the meeting except the announcement by the secretary that the 164th meeting of the American Physical Society would be in affiliation with Section B of the Pacific Division of the American Association for the Advancement of Science, at the University of Oregon, Eugene, Oregon, in the period from June 18 to 21, 1930.

Papers were presented in the morning from ten until twelve-thirty, and in the afternoon from one-thirty until four-thirty. There were no papers read by title, and the relatively short program gave ample time for discussion, making the meeting a great success.

Abstracts of the 18 papers presented are given in the following pages. An Author Index will be found at the end.

L. B. LOEB, *Local Secretary for the Pacific Coast*

ABSTRACTS

1. The blue-green absorption bands of Li_2. A. HARVEY AND F. A. JENKINS. *University of California.*—The absorption spectrum of lithium vapor contained in a nickel tube, and maintained at temperatures varying from 650°C to 900°C, has been examined under both high and low dispersion. Employing a tube 1 m long at the lower, temperatures, we have identified the band heads due to the less abundant isotope molecule, $Li^6 Li^7$, which accompany the (1,0), (2,0) and (3,0) bands of the stronger $Li^7 Li^7$ system. The isotope displacements agree with their calculated values within the error of measurment (calculated: 2.08, 4.32, 6.30A; observed: 2.06, 4.47, 6.37A. This checks the assignment of vibrational quantum numbers and the equations for the vibrational energy previously given (Phys. Rev. **34,** 1286 (1929)). Measurements of the band heads are necessarily inaccurate, because the head occurs at a low rotational quantum number. More satisfactory data may be obtained with the band lines, which are well resolved in the first order of the 15-foot grating. It has been possible to establish definitely that each band has the three-branch structure expected for a $^1\Pi \rightarrow {}^1\Sigma$ transition, by using an unambiguous graphical method due to Loomis (Phys. Rev. **32,** 223 (1928)). Quantitative measurements will be made of the alternating intensities previously reported, and the rotational isotope effect in the (0,0) band investigated.

2. Why does molecular hydrogen reach equilibrium so slowly? HARVEY HALL AND J. R. OPPENHEIMER, *University of California.*—The uncatalyzed conversion ortho-para in gaseous hydrogen may be investigated quantum mechanically. A molecule of parahydrogen may be converted by collision with any other molecule to orthohydrogen; but the probability for this

conversion is small, because the conversion is induced by the very small interaction of nuclear magnetic moment with the magnetic moment of the rotating molecule. Furthermore, two molecules of parahydrogen may be converted bo orthohydrogen by the interchange of nuclei between the molecules; this effect depends upon the overlapping of the wave functions for the nuclei which interchange; and its relative probability may be shown to be small, in comparison with the probability of a gas kinetic collision, of the order

$$e^{-(M/m)^{1/2}}$$

where M is the mass of the proton, and m that of the electron. The consideration of both effects shows that parahydrogen should, at N. P. T., be half convirted to orthohydrogen in a period of the order of 10^8 seconds.

3. The Carbon isoptoe, Mass 13. A. S. KING AND R. T. BIRGE. *Mount Wilson Observatory and University of California.*—A systematic study of the carbon isotope is in progress, with the following results to date. (1) The isotope has been found in the 2–0 (λ4382) band of C_2, and in the 1–0 (λ3590) band of CN, in addition to the original 1–0 band of C_2 and 0–0 band of CN. (2) Much stronger exposures of the 1–0 C_2 isotope band (λ4744) have been obtained, in both first and second order spectra, showing at least fifteen lines suitable for measuring the isotope shift. (3) The large perturbation in line P_{33} (λ4731.8) of the 1–0 C_2 band, does *not* appear in the corresponding isotope line, in agreement with theory. (4) The "staggering" in the main 1–0 C_2 band, caused by the absence of alternate rotational levels, is not present in the isotope band, again in agreement with theory. (5) The λ4744 isotope band, as excited in the furnace, is at least ten times as strong, relative to the main band, as in the arc, where it has not as yet been observed with certainty. The relative intensity of the isotope band is thus a *function of excitation conditions*, and this fact my well invalidate all estimates of relative isotope abundance, based on relative spectral intensity.

4. The vibrational isotope effect. RAMOND T. BIRGE. *University of California.*—Gibson (Zeits. f. Physik **50,** 692 (1928)) has formulated a beautiful method for calculating the vibrational isotope shift which is theoretically sound, and is the only accurate method available in the region of high values of the vibrational quantum number (n). The writer has added the details necessary for its precise numerical application, and has tested it on the absorption bands of Cl_2 previously treated by Elliott (Proc. Roy. Soc. **A123,** 629 (1929)), and of ICl, previously treated by Gibson (loc. cit.) and by Patkowski and Curtis (Trans. Faraday Soc. in press). In both these cases the theory is used to determine the correct n' numbering of the bands. The present results definitely require the half quantum numbers of the new mechanics. For Cl_2 they show that Elliott's n' numbering should be decreased by two units. For ICl they show, (1) that the main absorption progression arises from the $n''=0$ level, in apparent contradiction to a temperature experiment by Gibson (indicating the $n''=1$ level) which, however, the writer believes can be other wise explained: (2) that Gibson's n' numbering should be decreased by one unit. Both of these latter results agree with Patkowski and Curtis' conclusions, based on a less rigorous method of calculation.

5. Equivalent temperatures in the electric arc as measured by multiplet intensities. GEORGE R. HARRISON, *Stanford University.*—It has been shown by Langmuir, Nottingham, and others, that probe measurements in the positive column of the electric arc indicate equivalent electron temperatures lying between 5000 and 70,000A, the electrons having a Maxwellian velocity distribution. Engwicht and the writer have previously shown that corrections corresponding to temperatures in the neighborhood of 8000A had to be applied to the intensities of multiplets have widely separated upper states when measured in the titanium arc under average conditions. New studies have been made of the effect of changing excitation conditions on the relative intensities of multiplets in triads, and excitation temperatures between 3000 and 15,000A have been found for the positive column of the titanium arc. The curves relating current density and electron temperature are similar to those obtained by Nottingham with the Langmuir probe for cadmium, copper, and other arcs. While probably less accurate than the probe method, the intensity method gives an excellent check on its results. The most consistent data are obtained when multiplets with common lower states are chosen, so that the most accurate self-reversal corrections can be made if required.

6. Photographic photometry in the extreme ultra-violet. PHILIP A. LEIGHTON AND GEORGE R. HARRISON, *Stanford University.*—The work of one of us (J.O.S.A.**11**, 341 (1925)) on characteristics of photographic emulsions coated with fluorescent substances when exposed to ultra-violet light has been extended to the extreme ultra-violet. Slow, medium, and fast emulsions coated with various oils have been exposed in a vacuum spectrograph under controlled conditions. Several combinations have been found which exhibit uniform contrast throughout the region 1000–3,000A,with quite uniform sensitivity. The great difficulty of producing known variations of intensity in the extreme ultra-violet makes it desirable to find photographic materials which obey the reciprocity law accurately for use in this region. The best conditions to be fulfilled appear to be: 1. Selection of an emulsion obeying the reciprocity law accurately at wave-lengths near 4,000A; 2. Coating it with a substance which fluoresces near this wave-length, does not absorb its own fluorescence light, and completely absorbs in a thin layer all light of wave-lengths 1,000–3,000A. It is shown that the behavior of a given combination of emulsion and fluorescent substance in the extreme ultra-violet can often be predicted from a knowledge of the characteristics of each in the fluorescence region.

7. The broadening of spectrum lines during early stages of spark discharges. FRANK G. DUNNNIGTON AND ERNEST O. LAWRENCE. *University of California.*—The voltage across a spark gap drops to a relatively small value in 10^{-8} sec. after the beginning of the discharge. The cross-section of the discharge during periods of the magnitude of 10^{-7} sec. after break down, however, has not been observed, but there is evidence that it is small and therefore that the discharge current density is enormous. Such large initial ionic densities should be evidenced by large Stark effect broadening of spectrum lines in the early stages of sparks. Using the Beams electro-optical shutter we have photographed the light emitted by sparks during 5×10^{-7} sec. after breakdown. As expected all spectrum lines are diffuse, the spark doublets $(3d_{1,2}-4f)$ of Mg, $(3d_1-4f_1$, $(3d_2-4f_2)$ of Cd and Zn for example, having a breadth of approximately 40A. From existing data on the Stark effect of Mg it is calculated that the average ionic field producing the here observed Stark effect broadening is about 600,000 volts/cm, and that approximately 1/2 of the molecules in the path of the discharge are ionzed. The luminosity of the metallic vapor was observed to spread from the cathode at a velocity of 1.2×10^{-5} cm/sec.

8. The effective collision cross-section of cadmium and zinc atoms for slow electrons. ROBERT B. BRODE. *University of California.*—The variation with the electron velocity of the effective collision cross-section or the absorption coefficient, α,has been measured in the vapors of cadmium and zinc and found to follow a curve of the type previously found for mercury. (Proc. Roy. Soc. **125,** 134, (1929)). The cadmium curve has a maximum at about 40 volts. $\alpha=130$, and a minimum at about 25 volts, $\alpha=126$, followed by a steady rise with decreasing velocity to the limit of accurate measurements, 1 volt, $\alpha=700$. The zinc curve has a very flat maximum at about 50 volts, $\alpha=76$, a minimum at about 36 volts, $\alpha=74$, followed by a steady rise to $\alpha=500$ at 1 volt. As in mercury vapor a very small change in the general slope is observable in both of the curves just beyond the first resonance potential. The magnitude of the maximums are in the order ; Cd, $\alpha=125$; Zn, $\alpha=75$ and Hg, $\alpha=60$. Other related properties of these atoms such as the molar refractivity and the critical potentials show this same irregularity in order.

9. A direct measurement of molecular velocities. I. F. ZARTMAN, *University of California.* —The molecules whose velocities are to be measured are vaporized in an electrically heated crucible. A sharply defined molecular beam is formed by two rectangular slits, one of which is place in the cover of the crucible, the other 3.8 cm above the crucible slit. A steel cylinder, 9.41 cm inside diameter, which is rotated by an electric motor has a slit in its periphery and supports a glass collecting plate (which has been coated with a thin uniform deposit of the substance to be investigated) on the inner face diametrically opposite the slit. The entire assembly is operated in a vacuum of less than 10^{-4} mm and at speeds varying between 120 and 240 r.p.s. The molecules in the group entering the cylinder possess a distribution of velocities. These molecules pass to the opposite side of the cylinder and are collected on the glass plate in the form of a velocity spectrum whose density is measured with a microphotometer. The

velocity v of the molecules $=\pi d^2 n/s$ where d = diameter of the cylinder, n = r. p. s., and s = displacement of the molecules. Three runs taken with Bi at 800°C indicate that it vaporizes as a monatomic molecule. The displacement corresponding to the most probable speed in the beam at 120 r. p. s. is 0.7 cm. Other substances are now being investigated.

10. Experiments on the reported fine structure of the molybdenum K_β lines. SAMUEL K. ALLISON AND J. H. WILLIAMS. *University of California.*—Davis and Purks (Proc. Nat. Acad. Sci. **14,** 172, (1928)) have investigated the K-spectrum of molybdenum with a double x-ray spectrometer and obtained a complete resolution of the K_β doublet with both crystals reflecting in the second order. They report a new line K_β', 24 seconds of arc (0.17 X.U.) on the long wave-length side of $K_{\beta 1}$. The intensity of this new line appears to be about 1/3 that of $K_{\beta 1}$. An attempt has been made to study this new line using a double spectrometer with both crystals in the second order, and one in the second and one in the third order. Experiments were carried out at 42.7 kv and 45.6 kv. No positive evidence could be obtained for a satellite of $K_{\beta 1}$ in the reported position. From the curves obtained it appears that if such a satellite is present at the voltages stated above, its intensity must be less than 1/10 that of $K_{\beta 1}$. An average of eight determinations of the wave-length separation of β_1 and β_3 gives $\Delta\lambda = 0.572 \pm 0.003$ X.U. Previous values obtained with the single spectrometer were 0.563 X.U. (Allison and Armstrong, Phys. Rev. **26,** 701, (1925)) and 0.565 X.U. (Larsson, Phil, Mag. **3,** 1136, (1927)).

11. The electric space charge in the lower atmosphere. JOSEPH G. BROWN. *Stanford University.*—During the past year continuous records of space charge have been obtained 7.5 meters above the earth's surface. Obolensky's method of gathering all the ions from a known volume of air and measuring the residual charge has been used. The mean value of the positive charge has been about 0.10 E. S. U. per cubic meter. This value lies between Obolensky's and Kahler's. The air was quite free from dust which gives large negative charges, or smoke which gives large positive charges. If the air is still the space charge is remarkably constant, but if in motion sudden changes occur. This fact has led to the conclusion that most variations at a given point are due to different bodies of air which have different charges. At night when the air becomes saturated the positive space charge decreases and negative charge often occurs. During rain large positive or negative charge results. The mean diurnal variation is almost the reciprocal of the temperature variation, though there is a decided tendency to agree with the potential gradient. Sudden changes in space charge are accompanied by corresponding changes in potential gradient, though many changes in potential gradient are not accompanied by changes in space charge.

12. Variation of the electric potential gradient in the lower atmosphere. JOSEPH G. BROWN. *Stanford University.*—The mean electric field is characterized by a negative surface charge and a positive space charge. The mean distribution of the positive space charge can be inferred from the values of the potential gradient at different elevations, since $d^2V/dh^2 = -4\pi\rho$. Approximate computation shows that 50 percent of the charge is in the first kilometer, 18 percent in the second, etc., Variations in mean distribution will cause variations in potential gradient at any point by changing the relative magnitudes of the space charges (a) in horizontal layers and (b) in vertical columns. Expansions and convection currents will produce such changes in distribution and hence determine potential gradients. Continuous records of potential gradient and space charge have been obtained for a year 7.5 meters above the surface and their diurnal variations compared with the diurnal system of convection as inferred from the meteorological elements. In general upward currents near the surface correspond with increased charge and potential gradient, while downward correspond with decreased. General expansion and overflow above correspond with decreased charge and potential gradient, while cooling and inflow above correspond with increased. This is in agreement with the theory. Dust, smoke, and condensation are important factors but are believed to be of secondary importance in determining the mean diurnal variation.

13. The multiple crystal x-ray spectrograph. JESSE DUMOND AND HARRY KIRKPATRICK, *California Institute of Technology.*—An x-ray spectrograph designed to obtain increased intensity and contrast in spectra of scattered x-rays has been designed and built. The instrument consists of fifty small units each containing a Seeman wedge and calcite crystal. The units are closely spaced on the arc of a circle of one half meter radius and are oriented with great precision so that the spectra from the different units are exactly superposed. The spectra are photographed on a film bent to conform to an arc of the same circle. The geometry of the instrument is such that when the crystals are oriented so as exactly to superpose one spectral line from all of them, all wave-lengths and all orders are exactly in superposition. The instrument can take two forms having respectively a virtual point source and a real point source. The form having the virtual point source is the one here described. Beside the gain in intensity and contrast the instrument permits the study of scattered radiation over a wide range of scattering angles with almost perfect homogeneity of scattering angle.

14. Adjustments and tests of the multiple crystal x-ray spectrograph. HARRY KIRKPATRICK AND JESSE DUMOND, *California Institute of Technology.*—The technique of adjusting the crystals of the multiple crystal x-ray spectrograph is described and some improvements in design are suggested. Preliminary results obtained from a setting of seventeen of the crystals show that very good resolution is possible. The lines have a breadth of less than half an X.U. the dispersion being about 0.2 mm per X.U. The lines resulting from the superposition of seventeen crystals are not appreciably broader than the lines from one crystal and are seventeen times as intense showing that the superposition is practically complete. A preliminary test using the instrument to investigate the Compton effect for Mo K radiation scattered at 90 degrees from a paraffine scatterer with extremely homogeneous scattering angle confirms the result obtained by one of the authors for 180 degrees scattering that the so-called Compton line is diffuse. According to the work of Bergen Davis a fine line structure may be superposed on this broad diffuse structure though no theory has been yet given to account for such fine lines in the Compton shifted position. Attempts are being made to locate these lines with the multicrystal spectrograph.

15. Photographs of single crystals of ice, grown from the vapor. JOHN MEAD ADAMS, *University of California at Los Angeles.*—The abstract of this paper appears as a Letter to the Editor in this issue, p. 113.

16. Valence electrons in the diamond. M. L. HUGGINS AND RUTH PARRISH, *Stanford University.*—Previous calculations of density of scattering power for x-rays by means of Fourier series have involved the assumption that the structure can be resolved into two face-centered cubic structures, with the atoms oriented in the same way in both, and with three mutually perpendicular planes of symmetry passing through each atomic center. By taking the origin at a center of symmetry, midway between two atoms, this doubtful assumption need not be made. The resulting curves of density of scattering power show a small peak midway between each two neighboring carbon atoms. These peaks may be due to the electron pairs constituting the valence bonds.

17. A method of calculating complex spectra. WILLIAM V. HOUSTON, *California Institute of Technology.*—It is possible to build up, in a step by step process, the proper functions to represent any spectral term in the zero approximation. The coefficients occurring in these functions can be determined once for all by solving a set of simple simultaneous equations. From these functions, it is easy to compute the first approximation to the energy levels by integration over radial functions and spherical harmonics. If the radial integrals are not carried out, the integrals over the spherical harmonics still suffice to determine a number of relationships between the energies of the various multiplets. The accuracy of the determination is best when there are no other electron configurations with nearly the same energy as the one under consideration. The step by step process of setting up the functions gives at once the correlation between atomic terms and the ionic terms with which they are associated. It is then possible to apply the electron spins as a further perturbation. This leads to a determination of relationships between interval ratios in a multiplet and the interval ratios between multiplets.

18. The mobilities of gaseous ions in Cl_2 and Cl_2-air mixtures. LEONARD B. LOEB, *University of California.*—Work of the early investigators and of Herbert Mayer indicates that the presence of traces of Cl_2 reduces the mobility of the negative ion below that of the positive ion, a fact which appeared inconsistent with a theory of Condon and Loeb. No other investigations of mobilities of *both* ions in pure Cl_2 had been undertaken. The possibility that the discrepancy between theory and observation in earlier work was caused by HCl made a more careful investigation imperative. Cl_2 carefully prepared by heating $CuCl_2$ and free from both HCl and H_2O was used. It was found that the values of the mobilities in pure Cl_2 on the new absolute standard for positive and negative ions was 0.654 and 0.510 cm/sec per volt/cm respectively. A study of mixtures of dry air and Cl_2 showed that traces of Cl_2 less than 0.1 percent reduce the negative mobility below that of the positive ion. The positive mobilities were little affected by the presence of Cl_2, so that positive ions obey Blanc's law in Cl_2-air mixtures, indicating the absence of disturbances due to dipole moments in Cl_2 as is to be expected. The behavior of the negative ion shows a clustering effect of considerable magnitude which has no simple electrochemical explanation.

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